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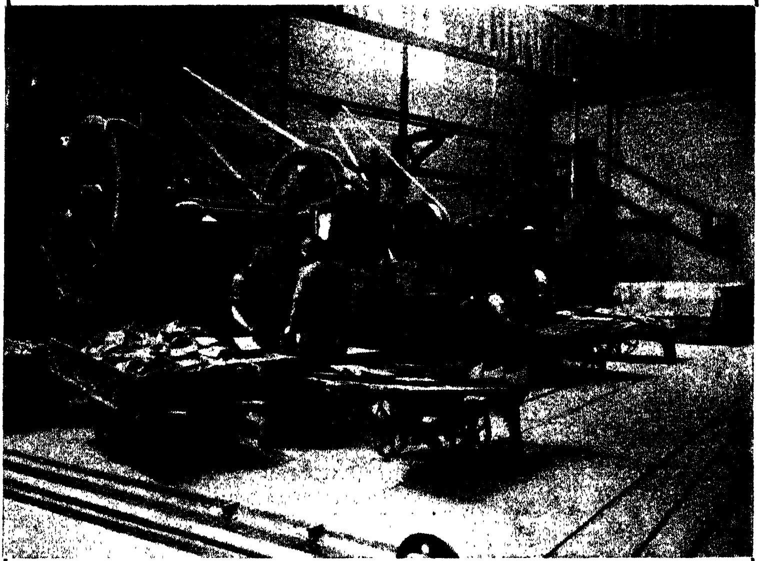

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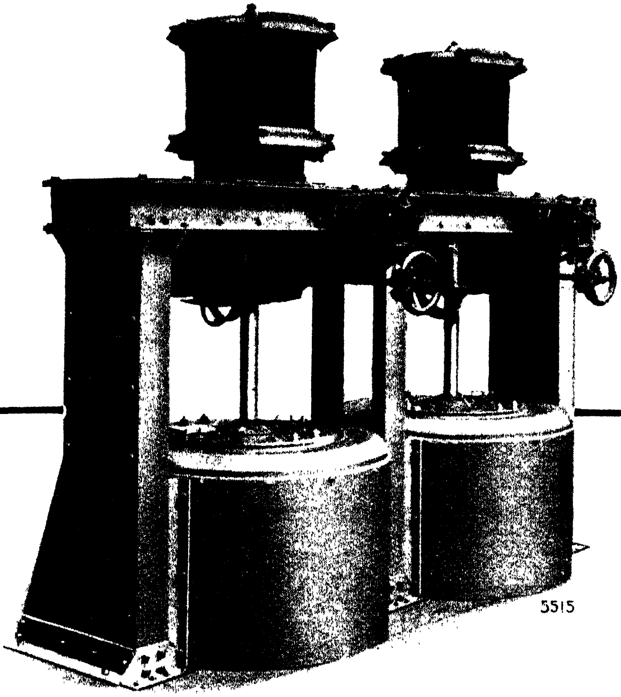

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Abbreviated Title.	FULL TITLE.
A.	Abstracts in Journal of the Chemical Society (until 1925) or in British Chemical Abstracts,* Section A.
Acta Comm. Tartuensis	Acta et Commentationes Universitatis Tartuensis (Dorpatensis).
Acta Lit. Sci. Univ. Hung. Francisco-Joseph.	Acta Litterarum ac Scientiarum Regiae Universitatis Hungaricae Francisco-Josephinae.
Acta Physicochim. U.R.S.S.	Acta Physicochimica U.R.S.S.
Acta Phytochim.	Acta Phytochimica.
Amer. Inst. Min. Met. Eng.	American Institute of Mining and Metallurgical Engineers Publication.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Med. Sci.	The American Journal of Medical Sciences.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Public Health	American Journal of Public Health and the Nation's Health.
Amer. J. Trop. Med.	The American Journal of Tropical Medicine.
Amer. Min.	American Mineralogist.
Anal. Farm. Bioquím.	Anales de Farmacia y Bioquímica (Buenos Aires).
Anal. Fís. Quím.	Anales de la Sociedad Española Física y Química.
Analyst	The Analyst.
Angew. Chem.	Angewandte Chemie (formerly Zeitschrift für angewandte Chemie).
Annalen	Justus Liebig's Annalen der Chemie.
Ann. agron.	Annales agronomiques.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Ann. Chim. analyt.	Annales de Chimie analytique et de Chimie appliquée.
Ann. Chim. appl.	Annali di Chimica applicata.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. Reports	Annual Reports of the Chemical Society.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico Agraria Sperimentali di Roma.
Ann. Soc. sci. Bruxelles	Annales de la Société scientifique de Bruxelles.
Arch. Chim. Farm.	Archivio di (chimica) Farmacognosia e Scienze affini.
Arch. Hyg.	Archiv für Hygiene und Bakteriologie.
Arch. Int. Med.	Archives of Internal Medicine.
Arch. Mikrobiol.	Archiv für Mikrobiologie.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Schiff. Trop. Hyg.	Archiv für Schiffs- und Tropenhygiene, Pathologie und Therapie exotischer Krankheiten.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kemi, Min. Geol.	Arkiv für Kemi, Mineralogi och Geologi.
Astrophys. J.	The Astrophysical Journal.
Atti Congr. naz. Chim.	Atti del Congresso nazionale di Chimica pura ed applicata.
Atti R. Accad. Lincei	Atti (Rendiconti) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.

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* The year is not inserted in references to 1936.

Abbreviated Title.	FULL TITLE.
Austral. J. Exp. Biol.	Australian Journal of Experimental Biology and Medicine.
B.	British Chemical Abstracts,* Section B.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft.
Ber. Schimmel	Berichte der Schimmel & Co. Aktien-Gesellschaft Miltitz bei Leipzig über aetherische Oele, Riechstoffe, usw.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Biochim. Terap. sperim.	Biochimica e Terapia sperimentale.
Bol. Min. Agric., Rio de Janeiro	Boletim do Ministerio da Agricultura, Industria e Commercio (Brazil).
Boll. chim.-farm.	Bollettino chimico-farmaceutico.
Boll. Uff. Staz. sperim. Ind. Pelli	R. Stazione Sperimentale per l'Industria delle Pelli e delle Materie concianti, Bollettino Ufficiale.
Bot. Gaz.	The Botanical Gazette.
Bot. Ztg.	Botanische Zeitung.
Brit. Med. J.	The British Medical Journal.
Bul. Chim. Soc. Rômane	Buletinul de Chimie pură si applicată al Societătii Rômane de Chimie.
Bul. Soc. Chim. Rômania	Buletinul Societătii de Chimie din Rômania.
Bul. Soc. Ştiinţe Cluj	Buletinul Şocietătii de Ştiinţe din Cluj.
Bull. Acad. polonaise.	Bulletin international de l'Académie polonaise des Sciences et des Lettres.
Bull. Acad. Sci. Krakow	Bulletin international de l'Académie des Sciences (Krakow) (now Bull. Acad. Poloniase).
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Inst. Phys. Chem. Res. Japan	Bulletin of the Institute of Physical and Chemical Research, Japan.
Bull. Inst. Pin	Bulletin de l'Institute du Pin.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. Path. exot.	Bulletin de la Société de Pathologie exotique.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Soc. Sci. Liège	Bulletin de la Société royale des Sciences de Liège.
Bull. Torrey Bot. Club	Bulletin of the Torrey Botanical Club.
Canadian Chem. Met.	Canadian Chemistry and Metallurgy.
Canadian J. Res.	Canadian Journal of Research.
Canadian Med. Assoc. J.	The Canadian Medical Association Journal.
Časopis čzechoslov. Lék.	Časopis Československého Lékárnictva.
Cellulosechem.	Cellulosechemie.
Centr. Min.	Centralblatt für Mineralogie, Geologie, und Paläontologie.
Chem. and Ind.	Chemistry and Industry.
Chem. Erde	Chemie der Erde.
Chem. Fabr.	Die Chemische Fabrik.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vědu a Průmysl."
Chem. Obzor	Chemický Obzor.
Chem. Reviews	Chemical Reviews.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Chim. et Ind.	Chimie et Industrie.

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* The year is not inserted in references to 1935.

Abbreviated Title.	FULL TITLE.
Chimica e l'Ind.	La Chimica e l'Industria.
Coll. Czech. Chem. Comm.	Collection of Czechoslovak Chemical Communications.
Comm. Zurich Congr. Internat. Assoc. Test. Mat.	Communications of the New International Association for Testing Materials (First Meeting, Zurich, 1930).
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Acad. Agric. France	Comptes rendus hebdomadaires des Séances de l'Académie d'Agriculture de France.
Compt. rend. Acad. Sci. U.R.S.S.	Comptes rendus de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biology.
Contr. Boyce Thompson Inst.	Contributions from the Boyce Thompson Institute.
Cornell Univ. Agric. Expt. Sta. Mem.	Cornell University Agricultural Experiment Station Memoirs.
Current Sci.	Current Science.
Deutsche med. Woch.	Deutsche medizinische Wochenschrift.
Ergeb. exakt. Naturwiss.	Ergebnisse der exakten Naturwissenschaften.
Ernähr. Pflanze	Die Ernährung der Pflanze.
Finska Kem. Medd.	Finska Kemistsamfundets Meddelanden (Suomen Kemistiseuran Tiedonantoja).
Florida Agric. Exp. Sta. Bull.	Florida Agricultural Experiment Station Bulletin.
Fortschr. Chem. Physik	Fortschritte der Chemie, Physik und physikalischen Chemie.
Fortschr. Röntgenstrahlen	Fortschritte auf dem Gebiete der Röntgenstrahlen über Metallkunde und Röntgenmetallographie.
Gazzetta	Gazzetta chimica italiana.
Giorn. Chim. ind. appl.	Giornale di Chimica industriale ed applicata (now absorbed into La Chimica e l'Industria).
Hauszeit. V.A.W. u.d. Erftwerk A.G. Aluminium	Hauszeitschrift der V.A.W. und der Erftwerk A.G. für Aluminium.
Helv. Chim. Acta	Helvetica Chimica Acta.
Helv. Physica Acta	Helvetica Physica Acta.
Ind. chim.	L'Industria chimica, mineraria e metallurgica.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.)	Industrial and Engineering Chemistry: Analytical Edition.
Ind. Med. Gaz.	The Indian Medical Gazette.
Indian J. Physics	Indian Journal of Physics.
Inst. int. Chim. Solvay Conseil Chim.	Institut international de Chimie Solvay, Conseil de Chimie.
J.	Journal of the Chemical Society.
J. Agric. Chem. Soc. Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res.	Journal of Agricultural Research.
J. Amer. Ceramic Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Amer. Water Works Assoc.	Journal of the American Water Works Association.
J. Appl. Chem. Russia	Journal of Applied Chemistry, Russia (Zhurnal prikladnoi Chimii).
J. Biochem. Japan	Journal of Biochemistry, Japan.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Educ.	Journal of Chemical Education.
J. Chem. Physics	The Journal of Chemical Physics.
J. Chim. physique	Journal de Chimie physique.
J. Chinese Chem. Soc.	Journal of the Chinese Chemical Society.
J. Exper. Med.	Journal of Experimental Medicine.

Abbreviated Title.	Full Title.
J. Gen. Chem. Russia	Journal of General Chemistry (U.S.S.R.) (formerly chemical part of the Journal of the Physical and Chemical Society of Russia).
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Ind. Hygiene	Journal of Industrial Hygiene.
J. Inst. Metals	Journal of the Institute of Metals.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Marine Biol. Assoc.	Journal of the Marine Biological Association of the United Kingdom.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
J. Physiol.	Journal of Physiology.
J. Phys. Radium	Journal de Physique et le Radium.
J. Physical Chem.	The Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Austral. Chem. Inst.	Journal and Proceedings of the Australian Chemical Institute.
J. Proc. Roy. Soc. N.S.W.	Journal and Proceedings of the Royal Society of New South Wales.
J. Res. Nat. Bur. Stand.	Journal of Research of the National Bureau of Standards (formerly Bureau of Standards Journal of Research).
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (now Journal of General Chemistry, Russia).
J. Sci. Instr.	Journal of Scientific Instruments.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Victoria	Journal (Proceedings) of the Society of Chemical Industry, Victoria.
J. Soc. Glass Tech.	Journal of the Society of Glass Technology.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Jernk. Ann.	Jernkontorets Annaler.
K. Norske Vidensk. Selsk.	Kongelige Norske Videnskabers Selskabs (Forhandlingar).
Kautschuk.	Kautschuk. Zeitschrift für wissenschaftliche und technische Kautschuksforschung.
Kinz. no Kenk.	Kinzoku no Kenkyu.
Klin. Woch.	Klinische Wochenschrift.
Kolloid-Beih.	Kolloid-Beihefte.
Kolloidchem. Beih.	Kolloidchemische Beihefte (now Kolloid-Beihefte).
Kolloid-Z.	Kolloid-Zeitschrift.
Lancet	The Lancet.
Latvij. Univ. Raksti	Latvijas Universitātes Raksti, Kimijas Fakultates Serija.
Legk. Metal.	Legkie Metally (Light Metals).
Magyar Chem. Fol.	Magyar Chemiai Folyóirat (Hungarian Chemical Journal).
Med. Parasit. and Parasitic Dis.	Medical Parasitology and Parasitic Diseases (Moscow).
Mem. Coll. Sci. Kyōtō	Memoirs of the College of Science, Kyōtō Imperial University.
Mercks Jahresber.	Mercks Jahresbericht.
Met. Ital.	La Metallurgia Italiana.
Metallurg.	Metallurgia.
Metallwirt.	Metallwirtschaft, Metallwissenschaft, Metalltechnik.
Mikrochem.	Mikrochemie.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.

Abbreviated Title.	FULL TITLE.
Min. Syrie i Zvet. Metally	Mineralnoe Syrie i Zvetnye Metally.
Mitt. Berg. Hütten. Abt. Hochschule Sopron	Mitteilungen der berg- und hüttenmannischen Abteilung an der kgl. ungarischen Hochschule für Berg- und Forstwesen zu Sopron, Ungarn.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchungen und Hygiene.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nach. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss.	Die Naturwissenschaften.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
New Hamps. Agric. Exp. Sta. Tech. Bull.	New Hampshire Agricultural Experiment Station Technical Bulletin.
Oesterr. Chem.-Ztg.	Oesterreichische Chemiker-Zeitung.
Parasit.	Parasitology.
Per. Min.	Periodico di Mineralogia.
Pflugers Archiv	Archiv für die gesamte Physiologie des Menschen und der Tiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci.	Philippine Journal of Science.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Physikal. Z. Sovietunion	Physikalische Zeitschrift der Sowjetunion.
Phytopath. Z.	Phytopathologische Zeitschrift.
Planta	Zeitschrift für wissenschaftliche Biologie. Abteilung E. Planta. Archiv für wissenschaftliche Botanik.
Plant Physiol.	Plant Physiology.
Prace Zakladu Metall. Pol. Warsaw	Prace Zakladu Metallurgicznego Politechniki Warsawskiej.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. VI Congr. S. Afr. Sugar Tech. Assoc.	Proceedings of the Sixth Congress of the South African Sugar Technologists Association.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy of Japan.
Proc. Indian Acad. Sci.	Proceedings of the Indian Academy of Science.
Proc. Internat. Soc. Soil Sci.	Proceedings of the International Congress of Soil Science.
Proc. 2nd Internat. Cong. Soil Sci.	Proceedings of the 2nd International Congress of Soil Science.
Proc. Iowa Acad. Sci.	Proceedings of the Iowa Academy of Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam (Proceedings, English version).
Proc. Manchester Lit. Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotian Inst. Sci.	Proceedings of the Nova Scotian Institute of Science.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. Staff Meetings Mayo Clinic	Proceedings of the Staff Meetings of the Mayo Clinic.
Przemysl Chem.	Przemysl Chemiczny.

Abbreviated Title.	FULL TITLE.
Quart. J. Pharm.	Quarterly Journal of Pharmacy and Pharmacology.
Rec. Mal. Surv. India	Records of the Malaria Survey of India.
Rec. trav. chim.	Recueil des travaux chimiques Pays-Bas et de la Belgique.
Rep. Brit. Assoc.	Reports of the British Association for the Advancement of Science.
Rev. Fac. Cienc. quím., La Plata	Revista de la Facultad de Ciencias químicas (Universidad nacional de la Plata).
Rev. gén. Caoutchouc	Revue générale du Caoutchouc.
Rev. Mét.	Revue de Métallurgie.
Rev. Mod. Physics	Reviews of Modern Physics.
Rev. Sci. Instr.	Review of Scientific Instruments.
Riv. Min.	Rivista di Mineralogia e Cristallographia.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Rocz. Nauk roln. leśn.	Roczniki Nauk rolniczych i leśnych.
Schr. zentr. biochem. Forschungsinst. Nahr. Genussm. Moscow	Schriften des zentralen biochemischen Forschungsinstituts der Nahrungs- und Genussmittelindustrie (Moscow).
Schweiz. Apoth.-Ztg.	Schweizerische Apotheker-Zeitung.
Schweiz. med. Woch.	Schweizerische medizinische Wochenschrift.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Nat. Tsing Hua Univ.	Science Reports of the National Tsing Hua University.
Sci. Rep. Tôhoku Imp. Univ.	Scientific Reports, Tôhoku Imperial University.
Sci. Rep. Tokyo Bunrika Daigaku	Science Reports, Tokyo Bunrika Daigaku.
Sewage Works J.	Sewage Works' Journal.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. preuss. Akad. Wiss. Berlin	Sitzungsberichte der preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Smithsonian Miscell. Coll.	Smithsonian Miscellaneous Collection.
Soil Sci.	Soil Science.
Suomen Kem.	Suomen Kemistilehti Acta Chemica Fennica.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tech. Rep. Tôhoku	Technology Reports of the Tôhoku Imperial University.
Textile Res.	Textile Research.
Trans. Amer. Inst. Min. Met. Eng.	Transactions of the American Institute of Mining and Metallurgical Engineers.
Trans. Bose Res. Inst.	Transactions of the Bose Research Institute, Calcutta.
Trans. Electrochem. Soc.	Transactions of the Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Rubber Ind.	Transactions of the Institution of the Rubber Industry.
Trans. Kansas Acad. Sci.	Transactions of the Kansas Academy of Science.
U.S. Geol. Survey	United States Geological Survey (Bulletins).
U.S. Pub. Health Rep.	United States Public Health Service : Public Health Reports.
Ukrain. Chem. J.	Ukrainian Chemical Journal (Ukrainskiĭ Khemichniĭ Zhurnal).
Union Pharmaceut.	L'Union Pharmaceutique, Répertoire de Pharmacie : Archives de Pharmacie et Journal de Chimie médicale (réunis).
Verh. K. Akad. Amsterdam	Verhandlingen der Koninklijke Akademie van Wetenschappen te Amsterdam.
Verh. Schweiz. Nat. Ges.	Verhandlungen der schweizerischen naturforschenden Gesellschaft.

Abbreviated Title.	FULL TITLE.
Water Works Eng.	Water Works Engineering.
Wiss. Veröff. Siemens-Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie (now Angewandte Chemie).
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektrochem.	Zeitschrift für Elektrochemie (und angewandte physikalische Chemie).
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Mikrobiol.	Zeitschrift für Mikrobiologie (Moscow).
Z. Pflanz. Düng.	Zeitschrift für Pflanzenernährung und Düngung.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Z. Ver. deut. Zucker-Ind.	Zeitschrift des Vereins der deutschen Zucker-Industrie (now Z. Wirts. Zuckerind.).
Z. Vitaminforschung	Zeitschrift für Vitaminforschung.
Z. Wirts. Zuckerind.	Zeitschrift der Wirtschaftsgruppe Zuckerindustrie.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zavod. Lab.	Zavodskaya Laboratoriya.
Zentr. Bakt. Par.	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Zhur. Obs. Khim.	Zhurnal Obschtchey Khimii.

ERRATUM.

VOL. 30, 1933.

Page	Line	
133	7*	*for* " aryl-magnesium halides " *read* " aryl-mercurihalides."

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* From bottom.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

RADIOACTIVITY AND SUB-ATOMIC PHENOMENA.

DURING the year, very rapid progress has been made in the study of artificial disintegration. The transformations among the lighter elements have been in many cases so inter-related that one can speak of nuclear reactions and a nuclear chemistry. The energy relations have led to a new scale of nuclear mass, and the detection and measurement of excited levels in these atoms are the beginning of a stage in the "nuclear quantum physics" initiated by the relation of α- and γ-rays in former years. The use of neutrons as bombarding particles and the development of the "slow neutron" process have led to wide developments in transmutation among the heavier elements. Some progress has been made in the study of the β-ray transformation and of the penetrating radiation.

1. ISOTOPIC CONSTITUTION OF THE ELEMENTS.

In this field, work has continued with the mass spectrograph and by spectroscopic methods. The technique of the former consists largely in obtaining ions from recalcitrant elements, and A. J. Dempster [1] has introduced for this purpose a high-frequency spark between solid metal electrodes in a high vacuum. This source yields abundant ions from many elements, including Pt, Au, W, and Sn. Platinum examined by this method [2] gave isotopes at 192, 194, 195, 196, 198, the lightest being faint and 198 not so strong as the other three; palladium gave isotopes at 102, 104, 105, 106, 108, 110. Gold gave no trace of Au 199 and it is suggested that its accepted atomic weight is too high. Iridium gave 191 and 193, the latter being the more abundant.[3] Uranium gave one isotope at 235 with intensity $< 1\%$ of that due to U^{238}, and it is suggested that this substance is the parent of the actinium series.[4] Further evidence on the actinium problem is obtained from a chemical determination of the atomic weight of protoactinium by A. von Grosse.[5] F. W. Aston[6] has published new mass-spectrograph results on Hf, Th, Rh, Ti, Zr, Ca, Ga, Ag, Ni, Cd, Fe, In, and the mass-spectrograph has also been used to obtain values for the abundance ratio of isotopes of Li, K, and Rb.[7]

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[1] *Nature*, 1935, **135**, 542; *A.*, 677.

[2] A. J. Dempster, *ibid.*, p. 993; *A.*, 909.

[3] *Idem, ibid.*, **136**, 909; cf. B. Venkatesachar and L. Sibaiya, *ibid.*, p. 437; *A.*, 1295.

Spectroscopic Methods.—The study of hyperfine structure of spectral lines which show an isotope splitting and the investigation of band spectra now provide a more or less definite contribution to our knowledge of isotopes. For instance, in platinum the ratio of the abundance of Pt^{192}, Pt^{194}, Pt^{195}, Pt^{196} is given as — : 5 : 8 : 8 by B. Fuchs and H. Kopfermann[8] and as 2 : 10 : 13 : 16 by B. Venkatesachar and L. Sibaiya,[9] both sets of workers using photometry of the hyperfine structure of Pt II lines, while band spectra have been used to investigate the isotopes of cadmium, zinc (hydride bands),[10] and indium (iodide bands).[11]

Some additions have been made to the determinations of nuclear mechanical and magnetic moments by the methods discussed in the Report for 1934. The new determinations include holmium,[12] hafnium,[13] silver,[14] lanthanum,[15] and potassium.[16] The only important technical advance represented is a spectroscopic one, *viz.*, the use of absorption-spectrum lines taken with an atomic beam to avoid Döppler effect. Regularities in the distribution of nuclear mechanical moments among atoms of odd and even atomic numbers have been noticed by S. Tolansky.[17]

Among the lighter elements, the study of the nuclear transmutations which take place when these are bombarded with protons or deuterons has led to an interesting revision of nuclear masses. The necessity for revision was pointed out independently by H. A. Bethe[18] and by M. L. E. Oliphant, A. E. Kempton, and (Lord) Rutherford.[19] In nuclear reactions there is strong evidence that the law of conservation holds if mass and energy be regarded as equivalent. The energies involved in the transmutation of the H, He, and Li nuclei among themselves may be beautifully explained on this basis,[20] the masses for the nuclei being taken from the mass-spectrograph work of Aston and of Bainbridge. If we regard the nucleus Be^9 as made up of two α-particles and a neutron, the mass assigned by K. T. Bainbridge[21] (9·0155; $O^{16} = 16{\cdot}000$) exceeds that of the components (8·0043[22] + 1·0080[23]) by the equivalent of about 3 M.E.V.* and the Be^9 nucleus should therefore be unstable.

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[4] A. J. Dempster, *Nature*, 1935, **135**, 180; *A.*, 1048; A. von Grosse, *J. Physical Chem.*, 1934, **38**, 487; *A.*, 1934, 578.

[5] *J. Amer. Chem. Soc.*, 1934, **56**, 2501; see also these Reports, p. 146, and review by G. Elsen, *Chem. Weekblad*, 1935, **32**, 343; *A.*, 910.

[6] *Proc. Roy. Soc.*, 1935, [*A*], **149**, 396; *A.*, 802.

[7] H. Bondy, G. Johannsen, and K. Popper, *Z. Physik*, 1935, **95**, 46; *A.*, 909; A. K. Brewer and P. D. Kueck, *Physical Rev.*, 1934, [ii], **46**, 894; *A.*, 1935, 140.

[8] *Naturwiss.*, 1935, **23**, 372; *A.*, 909.

[9] *Proc. Indian Acad. Sci.*, 1935, **2**, *A*, 101; *A.*, 1185.

[10] G. Stenvinkel and E. Svensson, *Nature*, 1935, **135**, 955; *A.*, 802.

[11] M. Wehrli, *Helv. Physica Acta*, 1934, **7**, 611; *Chem. Zentr.*, 1934, ii, 2953; *A.*, 1935, 558; cf. *A.*, 1934, 1286.

[12] H. Schüler and T. Schmidt, *Naturwiss.*, 1935, **23**, 69; *A.*, 424.

[13] E. Rasmussen, *ibid.*; *A.*, 424.

[14] H. Hill, *Physical Rev.*, 1935, [ii], **48**, 233; *A.*, 1183.

[15] M. F. Crawford and N. S. Grace, *ibid.*, **47**, 536; *A.*, 676.

[16] D. A. Jackson and H. Kuhn, *Proc. Roy. Soc.*, 1935, [*A*], **148**, 335; *A.*, 555.

[17] *Nature*, 1935, **135**, 620; *A.*, 676.

No spontaneous disintegration had, however, been found by careful experiments.[24] Further, the energy of the α-particles obtained when Be is bombarded with protons

$$_4Be^9 + {}_1H^1 \longrightarrow {}_3Li^6 + {}_2He^4$$

is much less than that calculated from the mass data of Bainbridge and of Aston.[19] A separate experiment showed that the excess energy was not radiated as a γ-ray. Similar difficulties arise in connexion with the α-particles obtained by bombarding beryllium with deuterons

$$_4Be^9 + {}_1H^2 \longrightarrow {}_3Li^7 + {}_2He^4$$

and in the case of boron bombarded with protons.[25]

Oliphant, Kempton, and Rutherford[19] point out that in the mass-spectrograph determinations the masses of H^1, H^2, Li^6, and Li^7 were determined by comparison with He^4, whereas those of Be^9, B^{10}, and B^{11} were determined by comparison with O^{16} with differences determined with reference to H^1. A small error in the mass ratio He^4/O^{16} would give a cumulative error in the masses of the other elements. By assuming a small error in this ratio and applying a corresponding correction to the mass-spectrograph data, it is possible to obtain a set of masses which agree much better with transmutation data. F. Kirchner and H. Neuert [26] had previously suggested a revision of the mass of Be^9 to fit in with their transmutation data. Bethe [18] pointed out that the excited C^{12} nucleus with 4·8 M.E.V. extra energy was still stable against disintegration into three α-particles, while the masses given by Aston would necessitate instability at a much lower excitation energy. He drew up a new scheme of masses for the elements up to O^{17}, and suggested a revision of the He^4/O^{16} ratio. The new atomic masses are given in Table I. F. W. Aston [27] has redetermined the masses of some of the light nuclei and has found values in better accord with the masses deduced from energy changes.

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[18] *Physical Rev.*, 1935, [ii], **47**, 633.

[19] *Proc. Roy. Soc.*, 1935, [*A*], **150**, 241; *A.*, 910.

[20] *Idem, ibid.*, **149**, 406; *A.*, 803.

[21] *Physical Rev.*, 1933, [ii], **43**, 367.

[22] F. W. Aston, *Proc. Roy. Soc.*, 1927, [*A*], **115**, 487.

[23] J. Chadwick and M. Goldhaber, *Nature*, 1934, **134**, 237.

[24] See, *e.g.*, E. Friedlander, *Compt. rend.*, 1935, **201**, 337; *A.*, 1185; R. D. Evans and M. C. Henderson, *Physical Rev.*, 1933, [ii], **44**, 59; *A.*, 1935, 141.

[25] D. M. Gans, W. D. Harkins, and H. W. Newson, *ibid.*, p. 310; *A.*, 1935, 141; F. Kirchner, *Physikal. Z.*, 1933, **34**, 897; *A.*, 1934, 128.

* M.E.V. signifies one million electron-volts here and throughout this Report.

TABLE I.

Revised Nuclear Masses based on Transmutation Data.

	Bethe.[18]	Oliphant *et al.*[19]	Aston, etc.
$_0n^1$	1·0085	1·0083	
$_1H^1$	1·0081	1·0081	1·0081 *
$_1H^2$	2·0142	2·0142	2·0148 *
$_1H^3$	3·0161	3·0161	3·0151
$_2He^4$	4·0034	4·0034	4·0041 *
$_3Li^6$	6·0161	6·0163	6·0175
$_3Li^7$	7·0169	7·0170	7·0176
$_4Be^9$	9·0135	9·0138	9·0164
$_5B^{10}$	10·0146	10·0143	10·0135
$_5B^{11}$	11·0111	11·0110	11·0121
$_6C^{12}$	12·0037	12·0027	12·0048
$_6C^{13}$	13·0069		13·0051
$_7N^{14}$	14·0076		14·0042
$_7N^{15}$	15·0053		15·0032
$_8O^{16}$	16·0000	16·0000	16·0000
$_8O^{17}$	17·0040		

Values marked * are from Aston.[27]

The study of artificial disintegrations has led to new precise values of a few other nuclear masses.[28] C. D. Ellis and W. J. Henderson [29] have shown that the upper limit of the β-ray or positron spectrum may be used to calculate the energy differences between the initial and final nuclei in a β-transition, and this reveals the possibility of determining a large number of nuclear masses, since the great majority of the artificial radioactive transformations are of this type. It should be pointed out that the exact nuclear masses are quantities of great importance, since they have a very direct connexion with the binding forces in the nucleus.

[26] *Physikal. Z.*, 1935, **36**, 54; *A.*, 277.
[27] *Nature*, 1935, **135**, 541; *A.*, 677.
[28] E. O. Lawrence, *Physical Rev.*, 1935, [ii], **47**, 17; *A.*, 277.
[29] *Proc. Roy. Soc.*, 1935, [*A*], **152**, 714.

The mass of the neutron which appears in this table rests upon several independent experimental results.[30] The transformation

$$_1H^1 + _0n^1 \longrightarrow _1H^2 + \gamma$$

with the new Aston masses [27] for H^1 and H^2 and the energy of the γ-ray determined by Fleischmann [31] gives a value 1·0083. P. I. Dee and C. W. Gilbert's investigation [32] of the reaction $_1H^2 + _1H^2 \longrightarrow _2He^3 + _0n^1$ enabled them to deduce the mass 1·0080 ± 0·0004. The neutron may therefore give a proton and an electron by an exothermic reaction

$$_0n^1 = _1H^1 + e + 0{\cdot}2 \text{ M.E.V.}^{33}$$

2. Nuclear Transmutation.

Work on the production of new atomic species by bombardment of elements with α-particles, protons, deuterons, and neutrons has continued during the year, so there is now a regular "nuclear chemistry." Many of the nuclei obtained are radioactive with half-life periods varying from 0·02 sec. to several months. In several cases, a given new nucleus can be obtained by several routes, and in many cases the new elements have been identified by chemical methods, *e.g.*, precipitation with appropriate reagents after the addition of an isotopic or homologous ion.

Following Fleischmann and Bothe,[31] we shall denote, *e.g.*, the reaction $_7N^{14} + _2He^4 \longrightarrow _8O^{17} + _1H^1$ as one of type $(\alpha; p)$. The expulsion of neutrons by α-particles then becomes a reaction of type $(\alpha; n)$. Protons may give reactions of types $(p; \alpha)$, $(p; n)$, or $(p; —)$ (capture). Deuterons give $(d; \alpha)$, $(d; n)$, and, rather frequently, $(d; p)$, while neutrons give $(n; \alpha)$, $(n; p)$, and $(n; —)$.

α-Particles.—No new $(\alpha; p)$ reactions giving rise to stable nuclei have been discovered, but several processes of this type, giving radioactive nuclei (Curie-Joliot type) have been reported. Silicon bombarded with α-rays gives a product of half-life 17—18 days, which is probably $_{15}P^{32}$ and gives electrons and not positrons on disintegration. The half-life and the absorption coefficient of the β-rays agree with those of $_{15}P^{32}$ obtained by bombarding $_{16}Si^{32}$ with neutrons.[34, 35] Magnesium bombarded with α-particles gives

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[30] Cf. ref. (23).

[31] *Z. Physik*, in the press; see also R. Fleischmann and W. Bothe, *Ergeb. exakt. Naturwiss.*, 1935, **14**, 1.

[32] *Proc. Roy. Soc.*, 1935, [*A*], **149**, 200; *A.*, 678.

[33] G. Wentzel, *Naturwiss.*, 1935, **23**, 35; *A.*, 278.

[34] H. Fahlenbrach, *ibid.*, p. 288; *A.*, 803.

[35] *Idem*, *Z. Physik*, 1935, **96**, 503; *A.*, 803.

several active elements, the most probable process being[34, 36, 37]

$$ {}_{12}\mathrm{Mg}^{25} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{13}\mathrm{Al}^{28} + {}_{1}\mathrm{H}^{1} $$
$$ {}_{13}\mathrm{Al}^{28} \longrightarrow {}_{14}\mathrm{Si}^{28} + e^{-} \ (\tau = 2{\cdot}1 \text{ m.}) $$

but the following reactions probably also take place :

$$ {}_{12}\mathrm{Mg}^{26} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{13}\mathrm{Al}^{29} + {}_{1}\mathrm{H}^{1} $$
$$ {}_{13}\mathrm{Al}^{29} \longrightarrow {}_{14}\mathrm{Si}^{29} + e^{-} $$
$$ {}_{12}\mathrm{Mg}^{24} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{14}\mathrm{Si}^{27} + {}_{0}n^{1} $$
$$ {}_{14}\mathrm{Si}^{27} \longrightarrow {}_{13}\mathrm{Al}^{27} + e^{+} $$

O. R. Frisch,[38] on bombarding sodium fluoride or lithium fluoride with α-particles, found an activity which he ascribed to Na^{22} formed by an $(\alpha ; p)$ process. The half life was $>$ 6 months, and the mean energy of the positrons was 0·2 M.E.V. Calcium gave a positron-emitting element, probably Sc^{43}, with a half period of about 4½ hours. This is the heaviest nucleus for which there is convincing evidence of disintegration of this type. A few further investigations have been made on previously known reactions. New determinations[39] of the halving period of radio-nitrogen, ${}_{7}\mathrm{N}^{13}$, give 11·0 and 10·73 minutes, which is identical with that of ${}_{7}\mathrm{N}^{13}$ obtained from ${}_{6}\mathrm{C}^{12}$ by $(p ; —)$ and $(d ; n)$ processes.

Several new processes of the type $(\alpha ; n)$ have been discovered. Silicon and phosphorus were found to give neutrons when bombarded with α-particles,[40] and O. Haxel[41] finds that nitrogen gives under fast α-bombardment a radioactive nucleus of half life 1·2 minutes in addition to the long-known $(\alpha ; p)$ transformation into stable O^{17}. The new nucleus is probably F^{17} produced by the reaction ${}_{7}\mathrm{N}^{14} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{9}\mathrm{F}^{17} + {}_{0}n^{1}$ (cf. p. 23). K. Schnetzler[42] has interpreted his results on the excitation function (see below) of lithium as indicating an excitation process without capture of the α-particle or emission of charged particles. P. Savel[43] has found evidence of a similar process in Li, N, Al, F. In the $(\alpha ; p)$ process

$$ {}_{5}\mathrm{B}^{10} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{6}\mathrm{C}^{13} + {}_{1}\mathrm{H}^{1} $$

the C^{13} nucleus may often be left in an excited state which emits a γ-ray, the proton carrying away less than the full energy of the transformation. This interpretation has been confirmed by a

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[36] C. D. Ellis and W. Henderson, *Nature*, 1935, **136**, 755.

[37] A. Eckhardt, *Naturwiss.*, 1935, **23**, 527; *A.*, 1049.

[38] *Nature*, 1935, **136**, 220; *A.*, 1186.

[39] C. D. Ellis and W. Henderson, *ibid.*, **135**, 429; *A.*, 559; H. Fahlenbrach, *Z. Physik*, 1934, **94**, 607.

[40] E. Amaldi, O. d'Agostino, E. Fermi, B. Pontecorvo, F. Rasetti, and E. Segrè, *Ric. Sci.*, 1935, **6**, [i], 11/12.

[41] *Z. Physik*, 1935, **93**, 400; *A.*, 426.

[42] *Ibid.*, **95**, 302; *A.*, 1049.

[43] *Ann. Physique*, 1935, [xi], **4**, 88; *A.*, 1049.

coincidence counter method by W. Bothe and H. J. von Baeyer.[44] A group of full-energy protons is also emitted, and these show no simultaneity with γ-ray emission.

Protons.—Considerable data have been accumulated on details of the disintegration of lithium, beryllium, boron, carbon, and fluorine by artificially accelerated protons; carbon alone gives an unstable product-nucleus, apparently by the simple capture reaction

$$\begin{gathered} {}_6C^{12} + {}_1H^1 \longrightarrow {}_7N^{13} + h\nu \\ {}_7N^{13} \longrightarrow {}_6C^{13} + e^{+} \end{gathered}$$ [45, 46]

The radioactive substance behaved physically like nitrogen [45] and gave a positron emission with an energy distribution extending up to about 1·1 M.E.V., which is in reasonable agreement with the values for N^{13} obtained by bombarding boron with α-particles (for identity of periods, see ref. 39). The "capture γ" radiation was detected:[46] it was "hard" but was too weak to be examined in detail. The γ-rays produced in the bombardment of boron [47] and lithium [48] by protons have been examined by measuring the energy of recoil electrons in a cloud chamber. The energies in the case of boron go up to about 14·5 M.E.V. and are ascribed to the reaction $B^{11} + H^1 \longrightarrow C^{12}$. The lower energies present may be due to an alternative process $B^{11} + H^1 \longrightarrow 3He^4$ or to a step-wise relaxation of a C^{12} nucleus excited to 14·5 M.E.V. The possible existence of a 14·5-M.E.V. excited level in C^{12} raises interesting theoretical difficulties. In the case of lithium the capture γ radiation is found to show a complicated structure of discrete lines with energies up to 16 M.E.V. The reaction is supposed [49] to be $Li^7 + H^1 \longrightarrow He^4 + He^4$ and the γ-rays are due to excitation of the α-particles, which must have a series of energy levels between 0 and 16 M.E.V.[50]

The transmutation functions of α and p processes, *i.e.*, the variation of the probability of a transmutation with the energy of the bombarding particles, have been the object of special study. The bombarding particle may get inside the nucleus by passing over a potential barrier representing the repulsive forces of the nucleus or by a "resonance" process in which a particle with a definite special amount of energy is transmitted through the barrier. In the former case the transmission is calculated by Gamow's theory, which gives a monotonic, approximately exponential increase with energy of the incident particle; in the case of resonance, there are peaks in the transmission curve and therefore in the transmutation function. The results available up to October, 1934, have been used in a paper by E. C. Pollard,[51] in which the values deduced for the height of the potential barriers are tabulated, together with resonance levels. The barrier heights and resonance levels lie on a smooth curve when plotted against atomic number. The barrier height is not the same for α-particles and for protons. Resonance occurs both for α-particles and for proton transmutations; it is particularly well marked for proton-capture processes of the type ${}_6C^{12} + {}_1H^1 \longrightarrow {}_7N^{13} + \gamma$. This reaction shows two sharp resonances at 480 and 400 kv. The γ-ray emission from lithium bombarded by protons shows resonance at 450 and 850 kv., but these rays from beryllium similarly bombarded do not appear to show resonance.[52] A theoretical analysis has been made by G. Breit and F. L. Yost,[53] who find that the simple model of the nucleus as a potential well surrounded by a region of inverse-square field must be modified to account for the experimentally observed probability of capture in the case of carbon.

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[44] *Nach. Ges. Wiss. Göttingen*, 1935, **1**, 195; von Baeyer, *Z. Physik*, 1935, **95**, 417.

[45] J. D. Cockcroft, C. W. Gilbert, and E. T. S. Walton, *Proc. Roy. Soc.*, 1935, [*A*], **148**, 225; *A.*, 276.

[46] L. R. Hafstad and M. A. Tuve, *Physical Rev.*, 1935, [ii], **48**, 306; H. Neuert, *Physikal. Z.*, 1935, **36**, 629; *A.*, 1297.

[47] H. R. Crane, L. A. Delsasso, W. A. Fowler, and C. C. Lauritsen, *Physical Rev.*, 1935, [ii], **48**, 102.

[48] *Idem, ibid.*, p. 125; *A.*, 1186.

[49] M. L. Oliphant, E. S. Shire, and B. M. Crowther, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 922; *A.*, 1935, 7.

[50] C. C. Lauritsen and H. R. Crane, *Physical Rev.*, 1934, [ii], **46**, 537, 1109.

Deuterons.—The use of the H^2 nucleus (deuteron) as a bombarding particle has led to very interesting results.

The transmutations of nitrogen ${}_7N^{14} + {}_1H^2 \longrightarrow {}_6C^{12} + {}_2He^4$ [(d; α) process] and ${}_7N^{14} + {}_1H^2 \longrightarrow {}_7N^{15} + {}_1H^1$ [(d; p) process] have been studied by E. O. Lawrence, E. McMillan, and M. C. Henderson.[54] The existence of excited levels in the C^{12} and N^{15} nuclei gives rise to a complicated set of ranges among the products, since different amounts of energy may be taken up by the nuclei and radiated as γ-rays. The γ-rays emitted in these processes have been studied by the cloud-chamber recoil method,[55] and a set of γ-ray lines observed. These data may also be compared with the energies of the γ-rays observed in the reactions [56, 57]

$$B^{11} + H^2 \longrightarrow C^{12} + {}_0n^1$$

and

$${}_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1$$

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[51] *Physical Rev.*, 1935, **47**, 611; *A.*, 804.

[52] L. R. Hafstad and M. A. Tuve, *ibid.*, p. 506; **48**, 306; *A.*, 1297.

[53] *Ibid.*, p. 203; *A.*, 1186.

[54] *Ibid.*, **47**, 273; *A.*, 559.

[55] H. R. Crane, L. A. Delsasso, W. A. Fowler, and C. C. Lauritsen, *ibid.*, **48**, 100.

[56] *Idem, ibid.*, 1934, [ii], **46**, 1110.

[57] H. Becker and W. Bothe, *Z. Physik*, 1932, **76**, 421.

There is therefore good evidence of the existence of series of excited states in the light nuclei; in some cases there is doubt as to which product of a reaction gives rise to a γ-ray. T. W. Bonner and W. M. Brubaker [58] find, by studying the energy distribution of the neutrons, that the reaction ${}_3Li^7 + {}_1H^2 \longrightarrow 2{}_2He^4 + {}_0n^1$ may take place either as shown or with Be^8 as an intermediate nucleus. Li, Be, B, C, N, O, F, Na, Si, Al, Cu, and Pt all yield radioactive products under deuteron bombardment. The reactions with lithium, boron, and fluorine are probably of $(d; p)$ type: [59] they give β-emitting substances of short period.

Nitrogen gives [60] radioactive O^{15} and oxygen gives [61] radioactive F^{17} by $(d; n)$ processes, and the identity of the new radio-elements has been established by chemical tests. The case of Na^{24}, obtained by a $(d; p)$ process, on bombarding Na^{23}, has been studied exhaustively by E. O. Lawrence.[62] This substance may have extensive application, for it has a half life of 15·5 hours, and already in 1934 Lawrence prepared sources equivalent to about 1 mg. of radium. It gives electrons up to 1·2 M.E.V., and homogeneous γ-rays of 5·5 M.E.V.

The transmutation functions for deuteron bombardment have been studied by E. O. Lawrence, E. McMillan, and R. L. Thornton [63] with very important results. They find that the efficiency of the bombardment of sodium, silicon, and aluminium does not increase with the energy of the deuterons as rapidly as would be expected on the Gamow theory of a charged particle penetrating a potential barrier. The production of radioactivity in copper by deuterons accelerated to less than 3·6 M.E.V. was observed, and it is very remarkable, since the comparatively heavy nucleus is protected by a formidable potential barrier. The processes investigated are all of $(d; p)$ type, and a theory worked out by J. R. Oppenheimer and M. Phillips [64] explains the results on the view that the deuteron consisting of proton and neutron is deformed when it approaches a potential barrier, and the neutron may be captured by the nucleus without the proton penetrating the barrier. The theory rests on the relatively small binding energy, E, of proton and neutron in the deuteron, and this energy appears as a parameter in the formula obtained. The formula fits the experiments with E equal to about 2·2 M.E.V., which is in agreement with other estimates. It appears that quite heavy nuclei may be transformed by deuteron impact, and an artificial radioactivity produced in this way has been reported for platinum.

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[58] *Physical Rev.*, 1935, [ii], **48**, 742.

[59] Crane, Delsasso, Fowler, and Lauritsen, *ibid.*, **47**, 887, 971.

[60] E. McMillan and M. S. Livingston, *ibid.*, p. 452; *A.*, 559.

[61] H. W. Newson, *ibid.*, **48**, 790.

[62] *Ibid.*, **47**, 17; *A.*, 277. [63] *Ibid.*, **48**, 493. [64] *Ibid.*, p. 501.

Neutrons.—A few further experiments have been done directly on the atomic disintegrations produced by neutron bombardment, using the cloud chamber. W. D. Harkins, D. M. Gans, and H. W. Newson [65] have studied reactions which they consider to be

$$
\begin{gathered}
{}_{10}\mathrm{Ne}^{20} + {}_{0}n^{1} \longrightarrow {}_{8}\mathrm{O}^{17} + {}_{2}\mathrm{He}^{4} \\
{}_{9}\mathrm{F}^{19} + {}_{0}n^{1} \longrightarrow {}_{7}\mathrm{N}^{1} + {}_{2}\mathrm{He}^{4}
\end{gathered}
$$

The nucleus ${}_{7}\mathrm{N}^{16}$ appears to be radioactive. F. N. D. Kurie [66] used nitrogen in a cloud chamber and interpreted his results as showing capture of the neutron and emission of an α-particle. He suggests that N^{15} is formed by capture and disintegrates with a half life of about 10^{-20} sec. He finds that the kinetic energy of the products of disintegration is independent of the energy of the incident neutron, and suggests that in the capture of the neutron the excess energy is radiated away. This is different from the cases of disintegration produced by α-particles studied by Blackett in which energy is conserved, and Kurie suggests that it is characteristic of neutron disintegration. The reactions in which slow neutrons are captured by boron and lithium have been studied by J. Chadwick and M. Goldhaber,[67] and by H. J. Taylor and Goldhaber,[68] using a new method in which the tracks left by the particles in a photographic emulsion are examined with a microscope. The capture of neutrons by a number of elements with emission of γ-rays has also been observed. These reactions will be considered below.

An enormous mass of results has been accumulated on the production of radioactive nuclei by neutron bombardment: these are included in Table II. At the end of 1934, Fermi and his co-workers [69] discovered that the activation of a large number of elements was greatly increased by interposing a body of water or other hydrogen-rich substance around the source and the material to be irradiated. They correctly attributed the effect to the slowing down of the neutrons by collision with the hydrogen nuclei, and a great deal of work has been done on the mechanism of this action and the properties of slow neutrons.

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[65] *Physical Rev.*, 1933, [ii], **44**, 945; *A.*, 1933, 1225; 1935, [ii], **47**, 52; *A.*, 277.

[66] *Ibid.*, p. 97.

[67] *Nature*, 1935, **135**, 65; *A.*, 277; see also B. Kurtschatov, I. Kurtschatov, and G. Latichev, *Compt. rend.*, 1935, **200**, 1199.

[68] *Nature*, 1935, **135**, 341; *A.*, 426; H. J. Taylor, *Proc. Physical Soc.*, 1935, **47**, 873; *A.*, 1297.

[69] E. Amaldi, O. d'Agostino, E. Fermi, B. Pontecorvo, F. Rasetti, and E. Segré, *Proc. Roy. Soc.*, 1935, [*A*], **149**, 522; *A.*, 910; preliminary reports in *Ric. Sci.*, 1934, **2**, 280, 380, 381, 467; 1935, **1**, 123; O. d'Agostino, *Gazzetta*, 1934, **64**, 835; *A.*, 1935, 276.

In many cases the radio-elements formed by neutron bombardment have been identified by chemical tests.[69] It will be seen from Table II that by far the most common reaction is a simple capture of the neutron, giving an isotopic nucleus one unit heavier. This seems always to be the case when the activation is enhanced by water, and is therefore due to slow neutrons. The capture is often accompanied by γ-emission, which may include γ-rays of very high energy.[70] In some cases the capture can be demonstrated by the absorption of the slow neutrons, using a disintegrable substance as a detector, though the product of capture shows no radioactivity and is apparently a stable nucleus. This is the case with Cd and Y. In the cases of lithium and boron, the bombardment with slow neutrons gives rise to capture γ's and the emission of an α-particle. These reactions may be used to detect slow neutrons.

Some of the products of neutron bombardment are of special interest. Fermi and his associates[71] found that the products of bombardment of uranium with neutrons included radio-elements not isotopic with any known element, and which they ascribed to elements with $Z > 92$. A. von Grosse and M. S. Agruss[72] examined this view and concluded that it was not valid, but that the elements were isotopic with Pa^{91}. New evidence has been brought forward from the chemical side by O. Hahn, L. Meitner, and F. Strassmann,[73] who show that the substance of half life 13 minutes is eka-rhenium with $Z = 93$, and the later paper of Fermi[69] not only produces new chemical tests but shows, by the identical water effects on the various active products, that they are probably products of successive transformation

$$_{92}\mathrm{U} + n \longrightarrow {}_{92}\mathrm{U} \longrightarrow \mathrm{A}_{93} + \beta \longrightarrow \mathrm{A}_{94} + \beta$$

The phenomenon of successive transformation is shown[74] by the series $\mathrm{Cl}^{37} + n \longrightarrow \mathrm{Cl}^{38}$; $\mathrm{Cl}^{38} \longrightarrow \mathrm{A}^{38} + e^-$; $\mathrm{A}^{38} \longrightarrow \mathrm{S}^{34} + \alpha^4$, and by the elements formed by the irradiation of thorium with neutrons.[75] The series is probably to be represented as

$$_{90}\mathrm{Th}^{232} + n \longrightarrow {}_{88}\mathrm{A}^{229} + \alpha^4 \xrightarrow[\text{1 min.}]{\beta} {}_{89}\mathrm{B}^{229} \xrightarrow[\text{11 mins.}]{\beta} {}_{90}\mathrm{C}^{229}$$

$$_{90}\mathrm{Th}^{232} + n \longrightarrow {}_{90}\mathrm{A}^{233} \xrightarrow[\text{30 mins.}]{\beta} \mathrm{A}^{233}$$

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[70] F. Joliot and L. Kovarski, *Compt. rend.*, 1935, **200**, 824.

[71] *Proc. Roy. Soc.*, 1934, **146**, 483; *A.*, 1934, 1284.

[72] *Physical Rev.*, 1934, [ii], **46**, 241; *J. Amer. Chem. Soc.*, 1935, **57**, 438.

[73] *Naturwiss.*, 1935, **23**, 544; *A.*, 1050.

[74] W. F. Libby, M. D. Peterson, and W. M. Latimer, *Physical Rev.*, 1935, [ii], **48**, 571.

[75] O. Hahn and L. Meitner, *Naturwiss.*, 1935, **23**, 320; *A.*, 910; (Mme.) I. Curie, H. von Halban, and P. Preiswerk, *Compt. rend.*, 1935, **200**, 1841, 2079; *A.*, 911, 1050; cf. ref. (69).

The chemical behaviour of the activity is consistent with this scheme and the elements belong to the hitherto-unknown radioactive series with $W = 4n + 1$. The rare earths have been investigated by S. Sugden,[76] G. von Hevesy and H. Levi,[77] and J. C. McLennan.[78] The activations of europium, dysprosium, and holmium are among the strongest which have been observed. There are some discrepancies which are probably due to the difficulties in separating these elements.

The Transmutation Function for Neutrons and the Speed of Slow Neutrons.—T. Bjerge and C. H. Westcott [79] examined various cases of artificial disintegration, using neutrons from different sources. They found that the reaction ${}_{15}P^{31} + {}_{0}n^{1} \longrightarrow {}_{13}Al^{28} + {}_{2}He^{4}$ could not be observed with neutrons of about 2 M.E.V. from the bombardment of deuterium with deuterons, while the reaction ${}_{15}P^{31} + {}_{0}n^{1} \longrightarrow {}_{14}Si^{31} + {}_{1}H^{1}$ was only reduced to one-third as compared with an equal number of neutrons from a Ra-Be source (up to 14 M.E.V.). Similar researches,[80] using as alternative sources the neutrons from Ra-Be and Ra-F (up to 4·5 M.E.V.), showed that the $(n; \alpha)$ activation of silicon and phosphorus did not occur with the slower neutrons, while the reactions ${}_{13}Al^{27} + {}_{0}n^{1} \longrightarrow {}_{12}Mg^{27} + {}_{1}H^{1}$, ${}_{15}P^{31} + {}_{0}n^{1} \longrightarrow {}_{14}Si^{31} + {}_{1}H^{1}$ did. P. Preiswerk [81] made similar investigations, using the neutrons from Ra + B (up to 6 M.E.V.), and found that the $(n; p)$ reactions with silicon, aluminium, and iron did not take place, while that with magnesium did. For a large number of transmutations, however, the yield is greatly increased by slowing the neutrons down in a hydrogen-rich material, and Fermi suggested that they were slowed down by multiple elastic collisions with hydrogen nuclei till they attained " thermal " velocities. The correctness of this view has been shown by P. B. Moon and J. R. Tillman's experiments,[82] in which the block of paraffin surrounding the test material was cooled with liquid air. The efficiency of activation in some cases was increased considerably, but the increase was not the same for all elements. The interpretation of the results is complicated by an increased absorption of the very slow neutrons in the paraffin itself. Similar results have been found by Fermi and others.[83] A direct proof of the velocities of the neutrons has been achieved by Fermi,[84] by O. R. Frisch, and by E. T. Sørensen,[85] who fastened source and test piece to a rotating wheel surrounded by paraffin and observed a kind of aberration effect, and by J. R. Dunning, G. B. Pegram, G. A. Fink, D. P. Mitchell, and E. Segré,[86] who used a toothed-wheel velocity selector with absorbing sectors of cadmium.

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[76] *Nature*, 1935, **135**, 469; *A.*, 559; J. K. Marsh and S. Sugden, *ibid.*, **136**, 102; *A.*, 1050.

[77] *Ibid.*, p. 103; *A.*, 1050.

[78] *Ibid.*, p. 831.

[79] *Ibid.*, 1934, **134**, 177, 286.

[80] I. Kurtschatov, L. Missovski, M. Eremejev, and G. Schtschepkin, *Physikal. Z. Sovietunion*, 1935, **7**, 257.

[81] *Compt. rend.*, 1935, **200**, 827; *A.*, 558.

[82] *Nature*, 1935, **135**, 904; **136**, 66; *A.*, 802, 1049; *Proc. Roy. Soc.*, **1936**, [*A*], **153**, 476.

[83] *Ric. Sci.*, 1935, **6**, 1, 11/12; see also J. R. Dunning, G. B. Pegram, G. A. Fink, and D. P. Mitchell, *Physical Rev.*, 1935, [ii], **47**, 796; **48**, 265; *A.*, 1186.

The mechanism of the slowing down of neutrons, the cross section of the hydrogen nucleus, etc., have been investigated by a number of workers.[87] It seems that the greater part of the slowing in hydrogen is due to elastic collisions. The efficiency of the slowing process is reduced with heavy water.[88] There is, however, another process by which neutrons can be slowed down, *viz.*, the excitation of a nucleus without capture of the nucleus.[89, 90, 91] It is found that screens of heavy metals, *i.e.*, gold or lead [90] or silver,[91] do increase the intensity of " water sensitive " reactions by this process.

The cross section for interaction of these slow neutrons with nuclei, as determined by the absorption method, is in many cases very large (3×10^{-20} cm.^{2} for gadolinium, 3×10^{-21} cm.^{2} for cadmium). It varies enormously from element to element, whereas the collision cross sections for fast neutrons lie on a fairly smooth curve when plotted against atomic numbers.[92] The cross section has been dealt with theoretically by several authors,[93] and Bethe has attempted a rather complete theory of the interaction of neutrons and nuclei, making a straightforward application of wave mechanics. The probability of capture may be large for slow neutrons on account of the long time they spend in the nucleus, and may be further increased by a resonance factor which cannot be predicted and varies from nucleus to nucleus. The theory shows (*a*) that a nucleus may have a large cross section for the elastic scattering of slow neutrons; (*b*) that capture with the emission of γ-rays may take place with large probability if there is a suitable vacant neutron level in the nucleus—in the absence of resonance the probability of capture decreases inversely as the velocity; (*c*) that disintegration with emission of α-particles may take place with high probability if the process is exothermic and the potential barrier opposing the exit of the α-particle is not too high—for this reason it is confined to light elements—$(n; p)$ disintegration is always endothermic and does not take place with slow neutrons; (*d*) that excitation without capture may also occur.

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[84] *Ric. Sci.*, 1935, **6**, No. 1, 11–12. [85] *Nature*, 1935, **136**, 258; *A.*, 1186.

[86] *Physical Rev.*, 1935, [ii], **48**, 704.

[87] R. Fleischmann, *Naturwiss.*, 1934, **22**, 839; *A.*, 1935, 41; T. Bjerge and C. H. Westcott, *Proc. Roy. Soc.*, 1935, [*A*], **150**, 709; *A.*, 1186; *Proc. Camb. Phil. Soc.*, 1935, **31**, 145; *A.*, 426.

[88] H. Herszfinkiel, J. Rotblat, and M. Zyw, *Nature*, 1935, **135**, 653; *A.*, 678; C. H. Collie, J. H. E. Griffiths, and L. Szilard, *ibid.*, p. 903.

[89] D. E. Lea, *ibid.*, 1934, **133**, 24; *Proc. Roy. Soc.*, 1935, [*A*], **150**, 637; *A.*, 1186; J. R. Dunning, G. B. Pegram, and G. A. Fink, *Physical Rev.*, 1935, [ii], **47**, 325; R. Fleischmann, see ref. (87); P. Auger, *Compt. rend.*, 1934, **198**, 365.

[90] L. Wertenstein, *Nature*, 1934, **134**, 970.

[91] W. Ehrenberg, *Nature*, 1935, **136**, 870; B. Kurtschatov, I. Kurtschatov, L. Missovski, and I. Roussinov, *Compt. rend.*, 1935, **200**, 1201.

[92] Dunning, Pegram, Fink, and Mitchell, *Physical Rev.*, 1935, [ii], **48**, 265.

[93] Amaldi *et al.*, see ref. (69); H. A. Bethe, *Physical Rev.*, 1935, [ii], **47**, 747; F. Perrin and W. Elsasser, *Compt. rend.*, 1935, **200**, 450; G. Beck and L. H. Horsley, *Physical Rev.*, 1935, [ii], **47**, 510.

This theory collates many of the known facts. It is, however, incomplete, since evidence is appearing that the cross section of different nuclei can vary in different ways with the neutron velocity. This appears strongly from the experiments of Moon and Tillman [82] and from those of Fermi and Amaldi,[94] in which an absorber is shown to absorb selectively (*a*) the neutrons which activate it and (*b*) some other bands of neutron energy.

γ-*Rays* (*Nucleur Photo-effect*).—The reactions ${}_1H^2 + h\nu \longrightarrow {}_1H^1 + {}_0n^1$, ${}_4Be^9 + h\nu \longrightarrow {}_4Be^8 + {}_0n^1$ have been confirmed and further studied.[95] Arzimovitch and Palibin find that the latter reaction does not proceed with γ-rays of energy less than 1·3 M.E.V.

Electrons.—Some reports have been made of an artificial radioactivity produced in aluminium by fast electron bombardment.[96] No activity was found by Livingood and Snell after 850-kv. bombardment, and this disintegration by electrons does not seem very likely.

TABLE II.

Nuclear Reactions and Radioactive Transformations of Light Nuclei (References in parentheses).

$${}_1H^1 + {}_0n^1 \longrightarrow {}_1H^2 + \gamma \ (89)$$
$${}_1H^2 + \gamma \longrightarrow {}_1H^1 + {}_0n^1 \ (95)$$
$${}_1H^2 + {}_1H^2 \longrightarrow {}_2He^3 + {}_0n_1 \ (33)$$
$${}_1H^2 + {}_1H^2 \longrightarrow {}_1H^3 + {}_1H^1 \ (33)$$

$${}_3Li^6 + {}_0n^1 \longrightarrow {}_1H^3 + {}_2He^4 \ (67)$$
$${}_3Li^6 + {}_1H^1 \longrightarrow {}_2He^3 + {}_2He^4 \ (49)$$
$${}_3Li^6 + {}_1H^2 \longrightarrow 2\,{}_2He^4 + \gamma \ (49)$$

$${}_3Li^6 + {}_2He^4 \longrightarrow {}_5B^9 + {}_0n^1 \ (98, 99). \quad B^9 \xrightarrow[1\text{ min.}]{e^+} Be^9$$

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[94] *Ric. Sci.*, 1935, **6**, ii, 9/10.

[95] J. Chadwick and M. Goldhaber, *Proc. Roy. Soc.*, 1935, [*A*], **151**, 479; *A.*, 1293; cf. *A.*, 1934, 1053; W. Gentner, *Compt. rend.*, 1935, **200**, 310; L. Arzimovitch and P. Palibin, *Physikal. Z. Sovietunion*, 1935, **7**, 245.

[96] M. Tanaka, *Physical Rev.*, 1935, [ii], **48**, 916; J. J. Livingood and H. H. Snell, *ibid.*, p. 851.

[97] Rutherford, Chadwick, and Ellis, "Radiations from Radioactive Substances," Cambridge, 1930.

[98] *Ann. Reports*, 1934. [99] *Ibid.*, 1933.

TABLE II. *cont.*

${}_3Li^7 + {}_1H^1 \longrightarrow 2\,{}_2He^4 + \gamma$ (49, 48)
${}_3Li^7 + {}_1H^2 \longrightarrow 2\,{}_2He^4 + {}_0n^1$ (49)
${}_3Li^7 + {}_1H^2 \longrightarrow {}_4Be^8 + {}_0n^1 \longrightarrow 2\,{}_2He^4 + {}_0n^1$ (58)

${}_3Li^7 + {}_1H^2 \longrightarrow {}_3Li^8 + {}_1H^1$ (49, 59). $Li^8 \xrightarrow[0\cdot5\text{ sec.}]{\beta} Be^8 \longrightarrow 2He^4$
${}_3Li^7 + {}_2He^4 \longrightarrow {}_3B^{10} + {}_0n^1$ (98, 99)
${}_3Li^7 + {}_2He^4$ (excitation) (42)

${}_3Li^7 + {}_2He^4 \longrightarrow Be^{10} + {}_1H^1$ (95). $Be^{10} \xrightarrow{\beta} B^{10}$?
${}_4Be^9 + \gamma \longrightarrow {}_4Be^8 + {}_0n^1 \longrightarrow 2He^4 + {}_0n^1$ (95)
${}_4Be^9 + {}_1H^1 \longrightarrow {}_5Be^{10} + \gamma$ (98)
${}_4Be^9 + {}_1H^1 \longrightarrow {}_3Li^6 + {}_2He^4$ (98)
${}_4Be^9 + {}_1H^6 \longrightarrow {}_5B^{10} + {}_0n^1 + \gamma$ (57)
${}_4Be^9 + {}_1H^2 \longrightarrow {}_3Li^7 + {}_1He^4$ (98)

${}_4Be^9 + {}_1H^2 \longrightarrow {}_4Be^{10} + {}_1H^1$ (98). $Be^{10} \xrightarrow{\beta} B^{10}$?
${}_4Be^9 + {}_2He^4 \longrightarrow {}_6C^{12} + {}_0n^1$ (98, 99, 57)

${}_5B^{10} + {}_0n^1 \longrightarrow {}_3Li^7 + {}_2He^4$ (67)

${}_5B^{10} + {}_1H^2 \longrightarrow {}_6C^{11} + {}_0n^1$ (98). ${}_6C^{11} \xrightarrow[20\text{ min.}]{e^+} {}_5B^{11}$
${}_5B^{10} + {}_1H^2 \longrightarrow {}_5B^{11} + {}_1H^1$ (98)
${}_5B^{10} + {}_1H^2 \longrightarrow 3\,{}_2He^4$ (98)

${}_5B^{10} + {}_2He^4 \longrightarrow {}_7N^{13}$ (98). ${}_7N^{13} \xrightarrow[11\text{ min.}]{e^+} {}_6C^{13*}$
${}_5B^{10} + {}_2He^4 \longrightarrow {}_6C^{13} + \gamma + {}_1H^1$ (97)
${}_5B^{11} + {}_1H^1 \longrightarrow 3\,{}_2He^4$ (98)
${}_5B^{11} + {}_1H^1 \longrightarrow {}_4Be^8 + {}_2He^4 \longrightarrow 3\,{}_2He^4$ (98)
${}_5B^{11} + {}_1H^2 \longrightarrow {}_6C^{12} + {}_0n^1 + \gamma$ (56)
${}_5B^{11} + {}_1H^2 \longrightarrow 3\,{}_2He^4 + {}_0n^1$ (98)
${}_5B^{11} + {}_1H^2 \longrightarrow {}_4Be^9 + {}_2He^4$ (98)

${}_5B^{11} + H^2 \longrightarrow {}_5B^{12} + {}_1H^1$ (59). ${}_5B^{12} \xrightarrow[0\cdot02\text{ sec.}]{\beta} C^{12}$

${}_6C^{12} + {}_1H^1 \longrightarrow {}_7N^{13} + \gamma$ (45, 46). ${}_7N^{13} \xrightarrow[11\text{ min.}]{e^+} {}_6C^{13*}$
${}_6C^{12} + {}_1H^2 \longrightarrow {}_7N^{13} + {}_1H^1$ (98) do.
${}_6C^{12} + {}_1H^2 \longrightarrow {}_6C^{13} + \gamma$ (98)
${}_6C^{12} + {}_1H^2 \longrightarrow {}_5B^{10} + {}_2He^4$ (98)
${}_7N^{14} + {}_0n^1 \longrightarrow {}_5B^{11} + {}_2He$ (98, 99)
${}_7N^{14} + {}_1H^1 \longrightarrow {}_6C^{11} + {}_2He^4$ (98)

${}_7N^{14} + {}_0H^2 \longrightarrow {}_8O^{15} + {}_0n^1$ (60). ${}_8O^{15} \xrightarrow[126\text{ sec.}]{e^+} N^{15}$
${}_7N^{14} + {}_6H^2 \longrightarrow {}_7N^{15} + {}_1H^1$ (54, 55)
${}_7N^{14} + {}_6H^2 \longrightarrow {}_6C^{12} + {}_2He^4$ (54, 55)

${}_7N^{14} + {}_2He^4 \longrightarrow {}_9F^{17} + {}_0n^1$ (41). ${}_9F^{17} \xrightarrow[1\cdot2\text{ min.}]{e^+} {}_8O^{17}$
${}_7N^{14} + {}_2He^4 \longrightarrow {}_8O^{17} + {}_1H^1$ (97)

${}_8O^{16} + {}_1H^1 \longrightarrow {}_9F^{17} + {}_0n^1$ (61). ${}_9F^{17} \xrightarrow[1\cdot2\text{ min.}]{e^+} {}_8O^{17}$

${}_9F^{19} + {}_0n^1 \longrightarrow {}_8O^{19} + {}_1H^1$ (59). ${}_8O^{19} \xrightarrow[40\text{ sec.}]{\beta} {}_9F^{19}$

${}_9F^{19} + {}_0n^1 \longrightarrow {}_9N^{16} + {}_2He^4$ (65). ${}_7N^{16} \xrightarrow[9\text{ sec.}]{\beta} {}_8O^{16}$
${}_9F^{19} + {}_1H^1 \longrightarrow {}_{10}Ne^{20} + \gamma$ (98)
${}_9F^{19} + {}_1H^1 \longrightarrow {}_8O^{16} + {}_2He^4$ (98)
${}_9F^{19} + {}_1H^2 \longrightarrow {}_{10}Ne^{20} + \gamma$ (98)
${}_9F^{19} + {}_1H^2 \longrightarrow {}_8O^{17} + {}_2He^4$ (98)

TABLE II. *cont.*

${}_{9}\mathrm{F}^{19} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{11}\mathrm{Na}^{22} + {}_{0}n^{1}$ (38). ${}_{11}\mathrm{Na}^{22} \xrightarrow[> 6 \text{ months}]{e^{+}} {}_{10}\mathrm{Ne}^{22}$

${}_{9}\mathrm{F}^{19} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{10}\mathrm{Ne}^{22} + {}_{1}\mathrm{H}^{1}$ (97)

${}_{10}\mathrm{Ne}^{20} + {}_{0}n^{1} \longrightarrow {}_{8}\mathrm{O}^{17} + {}_{2}\mathrm{He}^{4}$ (65, 99)

${}_{11}\mathrm{Na}^{23} + {}_{0}n^{1} \longrightarrow {}_{11}\mathrm{Na}^{24}$ (69). ${}_{11}\mathrm{Na}^{24} \xrightarrow[15 \text{ h.}]{\beta} {}_{12}\mathrm{Mg}^{24}$

${}_{11}\mathrm{Na}^{23} + {}_{0}n^{1} \longrightarrow {}_{10}\mathrm{Ne}^{23} + {}_{1}\mathrm{H}^{1}$ (69). ${}_{10}\mathrm{Ne}^{23} \xrightarrow[40 \text{ sec.}]{\beta} {}_{11}\mathrm{Fa}^{23}$

${}_{11}\mathrm{Na}^{23} + {}_{1}\mathrm{H}^{1} \longrightarrow {}_{10}\mathrm{Ne}^{20} + {}_{2}\mathrm{He}^{4}$ (27)

${}_{11}\mathrm{Na}^{23} + {}_{1}\mathrm{H}^{2} \longrightarrow {}_{11}\mathrm{Na}^{24} + {}_{1}\mathrm{H}^{1}$ (62). ${}_{11}\mathrm{Na}^{24} \xrightarrow[15 \text{ h.}]{\beta} {}_{12}\mathrm{Mg}^{24}$

${}_{11}\mathrm{Na}^{23} + {}_{1}\mathrm{H}^{2} \longrightarrow {}_{12}\mathrm{Mg}^{24} + {}_{0}n^{1}$ (62)

${}_{11}\mathrm{Na}^{23} + {}_{1}\mathrm{H}^{2} \longrightarrow {}_{10}\mathrm{Ne}^{21} + {}_{2}\mathrm{He}^{4}$ (62)

${}_{11}\mathrm{Na}^{23} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{12}\mathrm{Mg}^{26} + {}_{1}\mathrm{H}^{1}$ (97, 98)

${}_{11}\mathrm{Na}^{23} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{13}\mathrm{Al}^{26} + {}_{0}n^{1}$ (98, 99)

${}_{12}\mathrm{Mg}^{24} + {}_{0}n^{1} \longrightarrow {}_{11}\mathrm{Na}^{24} + {}_{1}\mathrm{H}^{1}$ (69). ${}_{11}\mathrm{Na}^{24} \xrightarrow[15 \text{ h.}]{\beta} {}_{12}\mathrm{Mg}^{24}$

${}_{12}\mathrm{Mg}^{24} + {}_{1}\mathrm{H}^{2} \longrightarrow {}_{11}\mathrm{Na}^{22} + {}_{2}\mathrm{He}^{4}$ (2)

${}_{12}\mathrm{Mg}^{24} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{14}\mathrm{Si}^{27} + {}_{0}n^{1}$ (36). ${}_{14}\mathrm{Si}^{27} \xrightarrow[1]{e^{+}} {}_{13}\mathrm{Al}^{27}$

${}_{12}\mathrm{Mg}^{24} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{13}\mathrm{Al}^{27} + {}_{1}\mathrm{H}^{1}$ (97)

${}_{12}\mathrm{Mg}^{25} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{13}\mathrm{Al}^{28} + {}_{1}\mathrm{H}^{1}$ (36). ${}_{13}\mathrm{Al}^{28} \xrightarrow[2{\cdot}1 \text{ min.}]{\beta} {}_{14}\mathrm{Sl}^{28}$

${}_{12}\mathrm{Mg}^{26} + {}_{0}n^{1} \longrightarrow {}_{12}\mathrm{Mg}^{27}$ (69). ${}_{12}\mathrm{Mg}^{27} \xrightarrow[\alpha]{\beta} {}_{13}\mathrm{Al}^{27}$

${}_{12}\mathrm{Mg}^{26} + {}_{0}n^{1} \longrightarrow {}_{10}\mathrm{Ne}^{23} + {}_{2}\mathrm{He}^{4}$ (69). ${}^{10}\mathrm{Ne}^{23} \xrightarrow[40 \text{ sec.}]{\beta} {}_{11}\mathrm{Na}^{23}$

${}^{12}\mathrm{Mg}^{26} + {}_{1}\mathrm{H}^{1} \longrightarrow {}_{11}\mathrm{Na}^{23} + {}_{4}\mathrm{He}^{4}$ (2)

${}_{12}\mathrm{Mg}^{26} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{13}\mathrm{Al}^{29} + {}_{1}\mathrm{H}^{1}$ (36). ${}_{13}\mathrm{Al}^{29} \xrightarrow{\beta} {}_{14}\mathrm{Si}^{27}$

${}_{13}\mathrm{Al}^{27} + {}_{0}n^{1} \longrightarrow {}_{13}\mathrm{Al}^{28}$ (69). ${}_{13}\mathrm{Al}^{28} \xrightarrow[2{\cdot}1 \text{ min.}]{\beta} {}_{14}\mathrm{Si}^{28}$

${}_{13}\mathrm{Al}^{27} + {}_{0}n^{1} \longrightarrow {}_{12}\mathrm{Mg}^{27} + {}_{1}\mathrm{H}^{1}$ (69). ${}_{12}\mathrm{Mg}^{27} \xrightarrow[10 \text{ min.}]{\beta} {}_{13}\mathrm{Al}^{27}$

${}_{13}\mathrm{Al}^{27} + {}_{0}n^{1} \longrightarrow {}_{11}\mathrm{Na}^{24} + {}_{2}\mathrm{He}^{4}$ (69). ${}_{11}\mathrm{Na}^{24} \xrightarrow[15 \text{ min.}]{\beta} {}_{12}\mathrm{Mg}^{24}$

${}_{13}\mathrm{Al}^{27} + {}_{0}\mathrm{H}^{1} \longrightarrow {}_{12}\mathrm{Mg}^{24} + {}_{2}\mathrm{He}^{4}$ (2)

${}_{13}\mathrm{Al}^{27} + {}_{1}\mathrm{H}^{2} \longrightarrow {}_{14}\mathrm{Si}^{28} + {}_{0}n^{1}$ (1)

${}_{13}\mathrm{Al}^{27} + {}_{1}\mathrm{H}^{2} \longrightarrow {}_{13}\mathrm{Al}^{28} + {}_{1}\mathrm{H}^{1}$ (1). ${}_{13}\mathrm{Al}^{28} \xrightarrow[2{\cdot}1 \text{ min.}]{\beta} \mathrm{Si}^{28}$

${}_{13}\mathrm{Al}^{27} + {}_{1}\mathrm{H}^{2} \longrightarrow {}_{12}\mathrm{Mg}^{25} + {}_{2}\mathrm{He}^{4}$ (1)

${}_{13}\mathrm{Al}^{27} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{15}\mathrm{P}^{30} + {}_{0}n^{1}$ (98). ${}_{15}\mathrm{P}^{30} \xrightarrow[3{\cdot}25 \text{ min.}]{e^{+}} {}_{14}\mathrm{Si}^{30}$

${}_{13}\mathrm{Al}^{27} + {}_{2}\mathrm{He}^{4} \longrightarrow {}_{14}\mathrm{Si}^{30} + {}_{1}\mathrm{H}^{1}$ (97, 98)

For elements of $Z > 13$, see Table III, but also :

${}_{14}\mathrm{Si}^{27} + {}_{2}\mathrm{He}_{4}{}^{4} \longrightarrow {}_{15}\mathrm{P}^{32} + {}_{1}\mathrm{H}^{1}$ (34)

${}_{20}\mathrm{Ca}^{40} + {}_{2}\mathrm{He}^{4} \longrightarrow \mathrm{Sc}^{43} + {}_{1}\mathrm{H}^{1}$. ${}_{21}\mathrm{Sc}^{43} \xrightarrow[4{\cdot}4 \text{ min.}]{e^{+}} {}_{20}\mathrm{Ca}^{43}$ (38)

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[1] E. McMillan and E. O. Lawrence, *Physical Rev.*, 1935, [ii], **47**, 343.

[2] M. S. Livingston, M. C. Henderson, and E. O. Lawrence, *ibid.*, 1933, [ii], **44**, 316.

TABLE III.

Artificial Radioactivity produced by Neutrons.

References not marked are to Fermi *et al.* (40, 69). The carrier of the activity and the half life are given. The mark * indicates that the activity is enhanced by water and is probably due to (*n*; —) transformation.

1	H	
2	He	
3	Li	
4	Be	
5	B	
6	C	
7	N	
8	O	
9	F	O^{19} 40 s., N^{16} 9 s.
10	Ne	
11	Na	Ne^{23} 40 s., Na^{24} 15 h.
12	Mg	Ne^{23} 40 s., Mg^{27} 10 m., Na^{24} 15 h.
13	Al	Al^{28} 2·3 m., Mg^{27} 10 m., Na^{24} 15 h. (cf. 97).
14	Si	Si^{31} 2·4 h., Al^{28} 2·3 m.
15	P	Al^{28} 2·3 m., Si^{31} 2·4 h.
16	S	P^{32} 14 d.
17	Cl	Cl 35 m., P^{32} 14 d.
18	A	
19	K	K^{42} 16 h.
20	Ca	Ca 4 h., K^{42} 16 h. (5)
21	Sc	K^{42} 16 h.
22	Ti	
23	V	V^{52} 3·75 m.
24	Cr	V^{52} 3·75 m.
25	Mn	Mn^{56} 2·5 h., V^{52} 3·75 m.
26	Fe	Mn^{56} 2·5 h.
27	Co	Co^{60} 20 m., Mn^{56} 2·5 h. (4)
28	Ni	Ni (? hr.), Co^{60} 20 m. (4)
29	Cu	Cu 5 m., Cu 10 h.
30	Zn	Cu 5 m., Cu 10 h., Zn* 100 m. (5)
31	Ga	Ga 20 m. ? 23 h.
32	Ge	30 m. ?
33	As	As^{76} 26 h.
34	Se	Se 35 m.
35	Br	Br 18 m., Br 4·2 h.
36	Kr	
37	Rb	
38	Sr	
39	Y	
40	Zr	Zr 40 h. (5)
41	Nb	
42	Mo	30 m. 36 h.
43	Ma	
44	Ru	40 s., 100 s., 11 h., 75 h. (8)
45	Rh	Rh 44 s., Rh 3·9 m.
46	Pd	Pd, Rh, ? 15 m.
47	Ag	Ag 22 s.*, Ag 2·3 m.
48	Cd	
49	In	In 54 m., In 3 h., ? 13 s. (Cf. 9).
50	Sn	
51	Sb	Sb 2·5 d.
52	Te	Te* 45 m.
53	I	I 25 m.
54	Xe	
55	Cs	Cs* 75 m. (7, 6)
56	Ba	Ba 80 m., ? 3 m.
57	La	1·9 d. (10)
58	Ce	
59	Pr	Pr* 19 h. (cf. 10)
60	Nd	
61	—	
62	Sm	40 m. (cf. 10)
63	Eu	9·2 h. (10)
64	Gd	8 h. none (10)
65	Th	3·9 h.
66	Dy	2·5 h. (10, 11)
67	Ho	2·6 h. (10), 35 h. (11)
68	Er	7 m., 1·6 d., 12 h. (11)
69	Tu	
70	Yb	3·5 h. (10, 11)
71	Lu	4·0 h.
72	Hf	Hf (months) (5)
73	Ta	
74	W	W 1d.
75	Re	Re 20 h.
76	Os	
77	Ir	Ir 19 h., 3 d. 50 m. (12)
78	Pt	? (13)
79	Au	Au 2·7 d.
80	Hg	
81	Tl	Tl* 97 m. (6)
82	Pb	
83	Bi	Bi (6)
84		
85		
86		
87		
88		
89		
90	Th	1 m., 24 m. (cf. p. 25).
91		
92	U	15 s., 40 s., 13 m., 100 m. (cf. p. 25).
93		

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[3] I. Kurtschatov, B. Kurtschatov, L. Missovski, G. Schtschepkin, and A. Vibe, *Compt. rend. Acad. Sci., U.R.S.S.*, 1934, **3**, 422.

[4] J. Rotblat, *Nature*, 1935, **136**, 515; *A.*, 1297.

[5] G. von Hevesy and H. Levi, *ibid.*, **135**, 580; *A.*, 678.

[6] J. C. McLennan, L. G. Grimmett, and J. Read, *Nature*, 1935, **135**, 505; *A.*, 678.

3. The β-Ray Disintegration.

Not much definite progress seems to have been made in testing the theories of β-decay which were described in last year's Report.[15] The Fermi theory has been criticised theoretically by R. L. Dolecek,[16] who develops a method allowing the calculation of the energy distribution of the β-electrons for any appropriate assumptions about the transfer of angular momentum from the nucleus to the emitted particles. He was unable to account for the shape of the β-ray energy distribution in the cases of the relatively heavy nuclei of potassium and rubidium, and supports the necessity for additional assumptions in the theory. E. J. Konopinski and G. E. Uhlenbeck[17] introduce a new weight factor into Fermi's treatment and find that the new distribution, which should hold strictly only for light nuclei, fits more satisfactorily to the experimental curves for the positrons from P^{30}, N^{13}, and the electrons from Al^{28}. The experimental data were provided by the work of C. D. Ellis and W. J. Henderson [18] and of A. J. Alichanov, A. J. Alichanian, and B. S. Dželepov,[19] and the agreement between the results of the two sets of workers was not very good, though both show the asymmetry which is a characteristic of the modified theory.

Much attention has been concentrated on the high-energy limit of the β-ray continua. The view was put forward by C. D. Ellis and N. F. Mott [20] that the upper limit of the continuum represents the energy available for the β-ray in every case of a given nuclear transition. When a β-ray of lower energy is emitted the surplus energy is carried off by a " neutrino." This view has been supported by the experiments of W. J. Henderson,[21] who used

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[7] W. M. Latimer, D. E. Hull, and W. F. Libby, *J. Amer. Chem. Soc.*, 1935, **57**, 781; *A.*, 678.

[8] I. Kurtschatov, L. Nemenu, and I. Selinov, *Compt. rend.*, 1935, **200**, 2162.

[9] L. Szilard and T. A. Chalmers, *Nature*, 1935, **135**, 98; *A.*, 271.

[10] S. Sugden, *ibid.*, p. 469; *A.*, 559; J. K. Marsh and S. Sugden, *ibid.*, **136**, 102; *A.*, 1049.

[11] G. von Hevesy and H. Levi, *ibid.*, p. 103; *A.*, 1050.

[12] L. Sosnowski, *Compt. rend.*, 1935, **200**, 922; *A.*, 678.

[13] *Idem*, *ibid.*, p. 446; *A.*, 426.

[14] *Idem*, *ibid.*, p. 1027; *A.*, 559.

[15] *Ann. Reports*, 1934, **31**, 394.

[16] *Physical Rev.*, 1935, [ii], **48**, 13; *A.*, 1048.

[17] *Ibid.*, pp. 7, 107; *A.*, 1048.

[18] *Proc. Roy. Soc.*, 1934, [*A*], **146**, 206.

[19] *Z. Physik*, 1935, **93**, 350; *A.*, 426.

[20] *Proc. Roy. Soc.*, 1933, [*A*], **141**, 502; *A.*, 1933, 1100; see also *Ann. Reports*, 1934, **31**, 394.

[21] *Proc. Roy. Soc.*, 1934, [*A*], **147**, 572; *A.*, 275; cf. P.C. Ho, *Proc. Camb. Phil. Soc.*, 1935, **35**, 119.

a coincidence Geiger counter in conjunction with a magnetic spectrograph to study the high-energy end of the thorium-*C* and -*C''* spectra. He found that the energy changes in the branched processes

$$\begin{tikzcd}
& \text{Th-}C' \arrow[dr, "\alpha"] & \\
\text{Th-}C \arrow[ur, "\beta"] \arrow[dr, "\alpha"'] & & \text{Th-}D \\
& \text{Th-}C'' \arrow[ur, "\beta"'] &
\end{tikzcd}$$

were equal if the upper limit were taken as the energy of the β-transformation and the γ-ray energy properly allowed for. Ellis and Henderson [22] studied the positrons from the artificial radioactive nucleus P^{30}, using an absorption method, and they assume that the upper limit of the spectrum gives the difference in energy between the ground states of P^{30} and its disintegration product Si^{30}, since no γ-rays were emitted in the disintegration. This assumption can be checked by equating the energies in the two sets of processes : [23]

$$\begin{aligned}
{}_{13}Al^{27} + {}_{2}He^{4} &= {}_{14}Si^{30} + {}_{1}H^{1} \\
{}_{13}Al^{27} + {}_{2}He^{4} &= {}_{15}P^{30} + {}_{0}n^{1} \\
{}_{13}P^{30} &= {}_{14}Si^{30} + \varepsilon^{+}
\end{aligned}$$

It is therefore probably true that the Ellis–Mott rule holds for both heavy and light nuclei, electron and positron emission. H. R. Crane, L. A. Delsasso, W. A. Fowler, and C. C. Lauritsen [24] drew the same conclusions by studying the electrons produced by bombarding boron with deuterons :

$$B^{11} + H^{2} \longrightarrow B^{12} + H^{1} \longrightarrow C^{12} + \varepsilon^{-} + H^{1}$$

The masses are here determinable by other nuclear reactions, and the upper limit lies at about 11 M.E.V.

The upper limiting energies have also been studied from the point of view of the empirical Sargent rule,[25] which connects the logarithm of the limiting energy with that of the decay period by one of two nearly linear relations. One of these is supposed to hold for "allowed" and the other for "forbidden" nuclear transitions.

The theory was also tested by F. N. D. Kurie, J. R. Richardson, and H. C. Paxton [26] with the electrons from radio-sodium, Na^{24}, and radio-silicon, and satisfactory agreements were obtained. The distributions obtained by Crane, Delsasso, Fowler, and Lauritsen [27] for the electrons obtained on bombarding lithium and fluorine with deuterons also fit the relation for the energy distribution. The experimental data on the artificially active elements are conflicting. Alichanov, Alichanian,[22] and Dželepov,[28] who have examined a number of elements, conclude that their results do not fit on the Sargent lines. An absorption estimate by Lawrence [29] of the maximum energy of the β-particles from radio-sodium, Na^{24} (1·2 M.E.V.), fits on the curve, and the results of Crane *et al.*[27] for the short-lived products of bombarding lithium (probably Be^8) and fluorine seem to fit fairly well. Kurie, Richardson, and Paxton [26] use a theoretical energy-distribution curve to estimate the end-points for C, Si, and Na. Na (2·1 M.E.V.) is in rather marked disagreement with Lawrence, and does not fit on the curve; silicon seems to fit tolerably well. The unpublished results of R. Naidu and R. E. Siday for rhodium, silver, and fluorine agree with the rule, but silicon, dysprosium, and europium do not; the probable errors are large, however. It is clear that the experiments are still inadequate.

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[22] *Proc. Roy. Soc.*, 1935, [*A*], **152,** 714.

[23] L. Meitner and R. Jaeckel, *Z. Physik*, 1934, **91,** 493.

[24] *Physical Rev.*, 1935, [ii], **47,** 887.

[25] For a recent modification, see G. J. Sizoo, *Nature*, 1935, **136,** 142 ; *A.*, 1048.

[26] *Physical Rev.*, 1935, [ii], **48,** 168. [27] *Ibid.*, **47,** 971.

The low-energy end of the β-ray spectrum of radium-*E* has been studied by H. O. W. Richardson,[30] who finds an unexpectedly large number of slow particles. It is uncertain how far these are of secondary origin. It has been pointed out that many modern views on the continuous β-spectrum require a neutrino to carry off unobserved a part of the energy, and a few further attempts [31] have been made to detect this particle. H. A. Bethe [32] has made a calculation of the ionising power of a neutrino possessed of magnetic moment, and in conjunction with the negative results of the experiments this shows that the magnetic moment cannot exceed 2×10^{-4} Bohr magneton.

4. THE POSITRON.

The positron was treated rather fully in last year's Report.[33] Positrons have been found in the cosmic radiation; positron–electron pairs are created by the transformation of the energy of hard γ-rays and perhaps fast electrons in the neighbourhood of an atomic nucleus, and they are annihilated by combination with an electron, with emission of radiation. During 1935, considerable attention was devoted to calculating the probability of production of a pair by *internal* conversion of a γ-ray emitted by a nucleus in its own atom.[34] Jaeger and Hulme calculate the internal conversion coefficient for element 84 for both dipole and quadruple transitions. There is in this case a marked difference between the average energies of the positrons and electrons emitted, the former having greater energies, while for light elements there should be a symmetric distribution of energies between the particles. The number of conversions predicted is in agreement with the results of A. J. Alichanov and M. S. Kosodaev [35] on the emission of positrons from radioactive sources. H. J. Bhabha [36] has calculated the probability of pair production by collision of charged particles.

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[28] *Nature*, 1935, **136**, 257; 1935, **135**, 393; *A.*, 426, 1186; see also ref. (19).

[29] *Loc. cit.*, ref. (62).

[30] *Proc. Roy. Soc.*, 1934, [*A*], **147**, 442; *A.*, 1935, 6.

[31] J. Chadwick and D. E. Lea, *Proc. Camb. Phil. Soc.*, 1934, **30**, 59; *A.*, 1935, 276; M. E. Nahmias, *ibid.*, 1935, **31**, 99; *A.*, 426; M. Wolfke, *Bull. Acad. Polonaise*, 1935, [*A*], 107; *A.*, 911.

[32] *Proc. Camb. Phil. Soc.*, 1935, **31**, 108; *A.*, 426.

[33] *Ann. Reports*, 1934, **31**, 397.

The annihilation radiation due to the combination of an electron and a positron has been studied experimentally by O. Klemperer,[37] who used the positrons from artificially radioactive elements and detected the radiation with two Geiger counters in a coincidence circuit. He found that in the normal annihilation process two γ-ray quanta are emitted in opposite directions. The energy available for each quantum is then $mc^2 = 0{\cdot}5$ M.E.V., and absorption measurements on the radiation were consistent with this. The annihilation has been dealt with theoretically by H. A. Bethe,[38] who calculates that a fast positron has rather a high probability of being annihilated during its motion, the energy being usually emitted as a pair of quanta (cf. ref. 37). There is, however, an appreciable probability of a single-quantum annihilation in the neighbourhood of a heavy nucleus. The annihilation of slowly moving positrons takes place almost entirely with emission of two quanta. (This process is the one which would have been observed in Klemperer's experiments.)

The part played by the annihilation process in the anomalous hard scattering of γ-rays is discussed by Bethe [38] and by E. J. Williams [39] and K. Tsu Tung.[40] The present view appears to be that the hard scattered radiation contains a broad band due to annihilation, since the annihilation radiation carries off the energy of motion of the positron as well as the annihilation energy itself. There is also present an important component due to the radiation emitted in the slowing down of Compton and pair electrons.

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[34] M. E. Rose and G. E. Uhlenbeck, *Physical Rev.*, 1935, [ii], **48**, 211; *A.*, 1187; J. R. Oppenheimer, *ibid.*, **47**, 144; *A.*, 278; J. C. Jaeger and H. R. Hulme, *Proc. Roy. Soc.*, 1935, [*A*], **148**, 708; *A.*, 557.

[35] *Z. Physik*, 1934, **90**, 249; *A.*, 1934, 1150.

[36] *Proc. Roy. Soc.*, 1935, [*A*], **152**, 559; cf. L. Nordheim, *J. Phys. Radium*, 1935, [vii], **6**, 135; *A.*, 677; L. Landau and E. Lifschitz, *Physikal. Z. Sowjetunion*, 1934, **6**, 244; *A.*, 677.

[37] *Proc. Camb. Phil. Soc.*, 1934, **30**, 347; *A.*, 279.

[38] *Proc. Roy. Soc.*, 1935, [*A*], **150**, 129.

[39] *Nature*, 1935, **135**, 266.

[40] *Sci. Rep. Nat. Tsing Hua Univ.*, 1935, **3**, **85**.

5. THE RADIOACTIVITY OF POTASSIUM.

The discovery of widespread neutron-induced radioactivity has enabled the problem of the natural activity of potassium and rubidium to be approached from a new angle. The activity of these elements is extremely weak, and it is now generally ascribed to rare isotopic constituents. Several papers[41] have appeared in which the activities are ascribed to K^{40} and Rb^{85}. These substances could have been formed in pre-terrestrial times by neutron bombardment of K^{39} and Rb^{85} and persist only in traces undetectable by the mass spectrograph. Von Hevesy finds that bombardment of scandium with neutrons gives K^{42} by the transition ${}_{21}Sc^{45} + {}_{0}n^{1} \longrightarrow {}_{19}K^{42} + {}_{2}\alpha^{4}$; K^{42} decays with a 16-hour period and is excluded as the naturally occurring radioactive constituent. K. Sitte[42] considers, on mass-energy grounds, that K^{40} should show a positron activity as well as the β-activity, and since he detects no positrons, he ascribes the potassium activity to K^{43}. Von Hevesy, however, finds that the assumption of K^{40} fits his data on the activity of the fractionated isotopes of potassium. Evidence for the existence of K^{40} has recently been found with the mass-spectrograph by A. O. Nier,[43] who finds $K^{40} : K^{39} = 1 : 8600$, and by A. K. Brewer,[44] who finds $K^{40} : K^{39} = 1 : 8300$. Even assuming that the activity is due to a rare isotope, the persistence of the activity over very long periods cannot be connected with the energy of the β-rays by the Sargent relation.[25] Klemperer considers that K^{40} probably has a large nuclear spin, and that the transition to Ca^{40} is a kind of " super-forbidden " one for which a low probability is to be expected.[45]

6. THE PENETRATING RADIATION.

Nothing has been discovered during the year to disturb the conclusion that the primary cosmic radiation consists mainly, and perhaps entirely, of charged particles. W. F. G. Swann[46] says that the variation of intensity with latitude, due to deviation in the earth's magnetic field, indicates that at least 25% of the incident radiation is of charged corpuscular type, and that the observations of the east–west asymmetry of the radiation in the equatorial region brings this value up to 31%. A. H. Compton,[47] relying largely on a balloon measurement of the cosmic rays in equatorial Java,[48] considers that at least 97% of the rays are charged, and an extrapolation of the data to the top of the atmosphere indicates that 99% are charged. Analyses of the general nature of the rays have been made by Compton [49] and by Swann. Compton attempted an analysis of the rays, starting with the intensity–height data obtained on balloon flights. When allowance has been made for the isotropic incidence of the rays on the top of the atmosphere, these curves show kinks which are interpreted as due to the successive removal of groups of particles of finite range. An application of the theory of the magnetic deviation of the particles in the earth's field gives the minimum energy which the particles must possess to reach the earth's atmosphere at all. Combining these data, and assuming (rather uncertain) relations between the range and energy of different kinds of fast particles, Compton ascribes one of his range groups to α-particles, one to electrons, and one to protons. The showers of particles detected with counter arrangements and in the Wilson chamber are regarded as produced by a secondary radiation. A difficulty in the theory lies in the fact that protons have not been distinguished in Wilson chamber photographs at sea level, though they should theoretically be present.

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[41] O. Klemperer, *Proc. Roy. Soc.*, 1935, [*A*], **148,** 638; G. von Hevesy, *Nature*, 1935, **135,** 96; *A.*, 276; A. Ruark and K. H. Fussler, *Physical Rev.*, 1935, [ii], **48,** 151; *A.*, 1185; F. H. Newman and H. J. Walke, *Nature*, 1935, **135,** 98, 508; *A.*, 677; *Phil. Mag.*, 1935, [vii], **19,** 767; G. von Hevesy, *Naturwiss.*, 1935, **34,** 583.

[42] *Nature*, 1935, **136,** 334.

[43] *Physical Rev.*, 1935, [ii] **48,** 283.

[44] *Ibid.*, p. 640.

[45] Cf. C. Hurst, *Nature*, 1935, **135,** 905.

[46] *Physical Rev.*, 1935, [ii], **48,** 641.

Swann considers that the charged particles which constitute the primary rays come right through the atmosphere; possibly not ionising directly, but producing long-range secondaries throughout their path. These secondaries are those observed in Geiger-counter measurements. The theory in this form gives an exponential law for the absorption of the measured radiation if we assume that the number of secondaries produced per unit length of primary path is proportional to the energy of the primary. The comparatively small departures from the exponential law may be explained by a distribution of the primary energy. The fact, discussed below, that showers and bursts increase more rapidly with altitude than the general radiation, is explained on the assumption that, although secondary production in *air* increases linearly with the energy of the rays, yet secondary production in *lead* increases more rapidly than this.

Extensive experimental work has been done on the cosmic radiation. The assumption usually made, that the coincidences of a set of Geiger–Müller counters in line represent the passage of a single ionising particle through the system, has been checked.[50] Absorption data for various materials have been obtained.[51] Auger and his co-workers interpret their results as indicating the presence of a hard and a soft component which may perhaps be identified with protons and electrons respectively.

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[47] Guthrie Lecture, *Proc. Physical Soc.*, 1935, **47**, 747.

[48] J. Clay, *Physica*, 1934, **1**, 363.

[49] A. H. Compton and H. A. Bethe, *Nature*, 1934, **134**, 134; see also ref. (47).

An analysis by C. G. and D. D. Montgomery [52] shows that there is no sharp distinction between the "showers" which discharge Geiger-counter systems and the large "Stösse" observed in ionisation chambers. Unpublished work by W. Ehrenberg and by H. Carmichael also tends to this conclusion. Several sets of experiments show that showers and bursts increase more rapidly than the general cosmic radiation with increase in altitude,[52, 53] and unpublished work in an aeroplane by H. J. J. Braddick and C. W. Gilbert shows this very markedly. These experiments either demand a special "shower-producing component" of the radiations, or they are to be explained along the lines indicated by Swann. A very recent paper by C. G. and D. D. Montgomery [54] indicates that the rate of burst production varies differently with altitude for different materials, and this produces severe difficulties for the "shower producing radiation" hypothesis. New data on the variation of shower production with thickness of material have appeared.[55] E. C. Stevenson and J. C. Street [56] have published photographs showing showers apparently produced in a lead plate by incident electrons. This is a new type of shower production, previous work having led to the conclusion that showers were always produced by a non-ionising radiation. T. H. Johnson [57] has continued work on the directional distribution of the cosmic rays, finding an unbalanced positively charged component of the incoming radiation.

H. J. J. Braddick.

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[50] J. C. Street, R. H. Woodward, and E. C. Stevenson, *Physical Rev.*, 1935, [ii], **47**, 891; *A.*, 1050.

[51] J. Clay, *Physica*, 1935, **2**, 645; *A.*, 1050; H. Tielsch, *Z. Physik*, 1934, **92**, 589; *A.*, 143; G. Alocco, *Nature*, 1935, **135**, 96; *A.*, 278; P. Auger, *Compt. rend.*, 1935, **200**, 739; *A.*, 560; P. Auger, A. Rosenberg, and F. Bertein, *ibid.*, p. 1022; *A.*, 560; P. Auger, L. Leprince-Ringuet, and P. Ehrenfest, *ibid.*, p. 1747; *A.*, 1050.

[52] *Physical Rev.*, 1935, [ii], **48**, 786.

[53] B. Rossi and S. de Benedetti, *Ric. Sci.*, 1934, **2**, 5, 95, 119; *A.*, 804; E. C. Stevenson and T. H. Johnson, *Physical Rev.*, 1935, [ii], **47**, 578; *A.*, 803; R. D. Bennett, G. S. Brown, and H. A. Rahmel, *ibid.*, p. 437; *A.*, 560; C. G. Montgomery and D. D. Montgomery, *ibid.*, p. 429; *A.*, 560.

[54] *Ibid.*, **48**, 969.

[55] J. E. Morgan and W. M. Nielsen, *ibid.*, p. 773.

[56] *Ibid.*, p. 464.

[57] *Ibid.*, p. 287.

GENERAL AND PHYSICAL CHEMISTRY.

1. INTRODUCTION.

THE choice of subjects in this Report has of necessity been dictated by personal, as well as by scientific, considerations. The chemistry of deuterium compounds continues to attract attention, and a report on this subject appears inevitable. The price of "heavy water" has fallen so considerably during the current year as to make the substance a relatively cheap reagent. Attention may be called to two publications: a review, with about 400 references, by H. C. Urey and G. K. Teal,[1] and a book by A. Farkas.[2] The successful separation of deuterium has stimulated interest in other isotopes, and it is not improbable that waters enriched with H^3 and with O^{18} will shortly be available for experimental investigation. Mention must be made of the fact that the artificial radioactive isotopes of light elements are already being used in the study of chemical and biological problems.

Articles on aspects of spectroscopy have appeared in the two previous Reports: in the present Report the spectra of polyatomic molecules and of deuterium compounds are the main considerations, since important advances have been made in these directions. The publication of two books on the subject likely to be of interest to chemists, by Frl. H. Sponer[3] and by R. de L. Kronig,[4] must be recorded.

Statistical methods for calculating thermodynamic functions have been known for some time, but only in recent years, as a result of developments in wave-mechanics and in spectroscopy, has it become possible to evaluate quantities of direct use to the chemist. The principles involved in the calculations have become especially important in the study of isotopic exchange processes and for theories of reaction velocity, and a report on the subject is overdue. The necessity for an annual report on chemical kinetics is obvious in view of the interest being taken in the subject by workers in such widely different fields of chemical activity. Two books on kinetics, by

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[1] *Rev. Mod. Physics*, 1935, **7**, 34.

[2] "Ortho-Hydrogen, Para-Hydrogen, and Heavy Hydrogen," Cambridge University Press, 1935.

[3] "Molekülspektren," Springer, Leipzig, 1935.

[4] "The Optical Basis of the Theory of Valency," Cambridge University Press, 1935.

F. O. Rice and K. K. Rice,[5] and by N. Semenoff,[6] have been published during 1935, and are likely to have an important influence.

There has been no specific consideration of surface chemistry for some years, and consequently certain aspects are discussed in the present Report. The enunciation of a theory of optical rotatory power, by M. Born,[7] which marks a definite advance, and the appearance of a book, likely to become a classic, by T. M. Lowry,[8] during the current year, indicated that a short review of optical activity, from the physical, rather than the organic, standpoint would not be out of place. Dipole-moment data have been used to determine the angles between the valency bonds, especially for oxygen and sulphur, but the situation has been confused: the introduction of new concepts has done much to clarify the position and it is now possible to consider the value and the limitations of the method.

In conclusion attention may be called to the issue of a new journal, in English, French, and German, *viz.*, the *Acta Physicochimica, U.R.S.S.* The Reporter feels that some apology is necessary for the omission of such topics as the quantum theory of valency, electron diffraction, photochemistry, the physical chemistry of surface films, and colloids, but these must be left for a subsequent occasion. S. G.

2. ISOTOPES.

Deuterium.—Separation. The electrolytic method of preparing deuterium has continued to attract attention, because, not only is it still the best means of obtaining the heavy isotope of hydrogen, but also the separation involves matter of great theoretical interest. A number of arrangements have been described for carrying out the electrolysis,[1] and although alkaline electrolytes have been mostly used, it appears that equally good results can be obtained with acid solutions.[2] The previous theoretical treatments [3] of the separation coefficient have been based on the view that an energy barrier prevents the passage of electrons from the cathode into the solution : it has now been shown that separation factors of the correct order, *viz.*, 10 ± 5, may be calculated by assuming the rate of production of gas on electrolysis to be dependent, at the current densities used, on the speeds of recombination of hydrogen and deuterium atoms, to form molecules, on the electrode.[4] It is becoming increasingly evident that the differing experimental values for *s* obtained under apparently identical conditions are due to variations in factors not yet fully understood which occur during the process of electrolysis.[5] For different metals, *s* appears to vary from 2·7 to 17 : there is no obvious connexion between the separation factor and the over-voltage of the cathode. Anodic prepolarisation of the latter increases *s*, and addition of α-naphthaquinone decreases it. By raising the *C.D.*, the value of *s* is generally increased, but this is not always the case.[6] A fundamental difficulty which may account for discrepant observations is the tendency towards the establishment of the equilibrium [7] $H_2 + HDO \rightleftharpoons H_2O + HD$, since this would lead to a factor of about 3·8 in every case. Slight variations in the catalytic activity of the electrode material for this process would bring about marked changes in the experimental results.

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[5] "Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, 1935.

[6] "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935.

[7] *Proc. Roy. Soc.*, 1935, [*A*], **150**, 84.

[8] "Optical Rotatory Power," Longmans, 1935.

[1] M. Harada and T. Titani, *Bull. Chem. Soc. Japan*, 1934, **9**, 457; *A.*, 1935, 44; E. W. Washburn, E. R. Smith, and F. A. Smith, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 599; *A.*, 1935, 175; P. Goldfinger and J. Scheepers, *J. Chim. physique*, 1934, **31**, 628; *A.*, 1935, 311; B. Kamieński, *Rocz. Chem.*, 1934, **14**, 401; *A.*, 1935, 311; W. G. Brown and A. F. Daggett, *J. Chem. Physics*, 1935, **3**, 216; *A.*, 723; H. C. Urey and M. H. Wahl, *Physical Rev.*, 1935, [ii], **45**, 566; *A.*, 1329; H. Erlenmeyer and H. Gärtner, *Helv. Chim. Acta*, 1935, **18**, 419; *A.*, 589.

As the deuterium content of the electrolyte is increased, *s* evidently tends towards the value required by the complete establishment of equilibrium, even at nickel cathodes. With only slightly enriched water, however, containing 1 part of deuterium oxide in about 3000 parts, a factor as high as 100 has been claimed, based on the assumption that normal water contains 1 part of deuterium oxide in 5500. This result [8] is of great importance, since theoretical considerations, in which the possibility of quantum-mechanical leakage through an energy barrier—the " tunnel effect "— is neglected, lead to the expectation of a value of *s* less than 20, whereas much higher factors should be possible if " tunnelling " can occur.[9] Although some authors[10] regard this as one of the first proofs that the leakage effect is an important factor in the reactivities of hydrogen and deuterium atoms, the conclusion must, for the present, be accepted with reserve. The high factor is based on the supposition that normal water contains 1 part of deuterium oxide in 5500, whereas a value of 1 to 4500 for the isotopic ratio would give a normal factor.[8] The proportion of 1 part in 9000 reported last year[11] appears to be definitely excluded by the new work, and even the proportions of 1 part of D_2O in 5000 or 6000 obtained from density measurements[12] and by the mass spectroscope[13] may eventually prove to be too low: experimental work of high precision is clearly necessary.

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[2] A. I. Brodski *et al.*, *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **3**, 615; *A.*, 1935, 44.

[3] *Ann. Reports*, 1934, **31**, 20; W. W. Sawyer, *Proc. Camb. Phil. Soc.*, 1935, **31**, 116 ; *A.*, 456.

[4] H. C. Urey and G. K. Teal, *Rev. Mod. Physics*, 1935, **7**, 44; O. Halpern and P. Gross, *J. Chem. Physics*, 1935, **3**, 452; *A.*, 1210; see also H. Eyring and J. Sherman, *ibid.*, 1933, **1**, 345.

[5] Private communication from Mr. J. H. Wolfenden.

[6] A. Eucken and K. Bratzler, *Z. physikal. Chem.*, 1935, **174**, 279.

[7] *Ann. Reports*, 1934, **31**, 16.

[8] M. P. Applebey and G. Ogden, *J.*, 1936, 163.

[9] C. E. H. Bawn and G. Ogden, *Trans. Faraday Soc.*, 1934, **30**, 432; *A.*, 1934, 602.

Further experiments on the fractional distillation of water have confirmed the possibility of enrichment in this manner.[14] Desorption of electrolytic hydrogen from charcoal at liquid-air temperatures gives a 3- to 5-fold,[15] and diffusion through palladium a 4-fold,[16] enrichment of deuterium over that originally present. Partial separation of hydrogen and deuterium also results because of the preferential adsorption of deuterium oxide vapour by charcoal and by silica gel.[17] The claim has been made[18] that, in spite of reports to the contrary,[19] in the formation of crystal hydrates there is some selectivity in favour of deuterium oxide.

Analysis. The thermal conductivity method for determining the deuterium content of hydrogen gas has been improved,[20] permitting of a precision of 0·02% with 0·5 c.c. of gas at 1 atm. Two new methods for estimating D/H ratios, depending on the measurement of the freezing point of water [17] and on observations of its vapour pressure,[21] have been described.

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[10] J. Horiuti and M. Polanyi, *Acta Physicochimica U.R.S.S.*, 1935, **2**, 522.

[11] (Mrs.) E. H. Ingold, C. K. Ingold, H. Whitaker, and R. Whytlaw-Gray, *Nature*, 1934, **134**, 661; *A.*, 1934, 1317.

[12] H. L. Johnston, *J. Amer. Chem. Soc.*, 1935, **57**, 484; *A.*, 590; A. J. Edwards, R. P. Bell, and J. H. Wolfenden, *Nature*, 1935, **135**, 793; *A.*, 841.

[13] W. Bleakney and A. J. Gould, *Physical Rev.*, 1933, **44**, 265; *A.*, 1933, 994.

[14] M. Harada and T. Titani, *Bull. Chem. Soc. Japan*, 1935, **10**, 39, 41; *A.*, 458; W. N. Christiansen, R. W. Crabtree, and T. H. Laby, *Nature*, 1935, **135**, 870; *A.*, 815; M. H. Wahl and H. C. Urey, *J. Chem. Physics*, 1935, **3**, 411; *A.*, 1064; N. Morita and T. Titani, *Bull. Chem. Soc. Japan*, 1935, **10**, 257; *A.*, 1087; P. Jaulmes, *Chim. et Ind.*, 1935, **33**, 1045; *B.*, 609; see also B. Kamieński, *loc. cit.*, ref. (1).

[15] H. S. Taylor, A. J. Gould, and W. Bleakney, *Physical Rev.*, 1933, [ii], **43**, 496; *A.*, 1934, 1316.

[16] O. Luhr and L. Harris, *ibid.*, 1934, [ii], **45**, 843; *A.*, 1935, 1336.

[17] A. King, F. W. James, C. G. Lawson, and H. V. A. Briscoe, *J.*, 1935, 1545.

[18] K. Okabe, M. Harada, and T. Titani, *Bull. Chem. Soc. Japan*, 1934, **9**, 460; *A.*, 1935, 48.

[19] H. Erlenmeyer and H. Gärtner, *Helv. Chim. Acta*, 1934, **17**, 970; *A.*, 1934, 1303; E. H. Riesenfeld and H. E. Riesenfeld, *Ber.*, 1934, **67**, [*B*], 1659; *A.*, 1934, 1327; see also *Ann. Reports*, 1934, **31**, 89.

[20] H. Sachsse and K. Bratzler, *Z. physikal. Chem.*, 1934, **171**, 331; *A.*, 1935, 20.

Exchange reactions. Studies of interchange reactions between deuterium and compounds containing hydrogen have been continued, partly because of their general interest and partly in order to elucidate reaction mechanisms. Direct introduction of deuterium into benzene has been observed [22] on shaking with 90% sulphuric acid of enhanced deuterium content : the significance of the result has been discussed.[23] Exchange also occurs with methyl- and dimethyl-amine,[24] as their hydrochlorides, when dissolved in deuterium-enriched water, and confirmation of the reaction between deuterium oxide in alkaline solution and acetylene has been claimed,[25] although it has been stated that exchange does not occur.[26] Slow exchange takes place between sodium acetate and deuterium oxide,[24] and a rapid interchange between hydrogen peroxide and deuterium oxide has been observed; [27] no reaction is noted when potassium hypophosphite is dissolved in water containing deuterium oxide.[27] Water obtained from the combustion of various carbohydrates, of natural origin, has been found to contain more deuterium than normal.[28] A number of hexoses and their glycosides, etc., have been observed to undergo isotopic exchange in 11—30% and in 80—96% deuterium oxide; the results indicate that all the hydroxyl groups take part in the exchange.[29] The investigation of the direct introduction of deuterium into acetone in aqueous alkaline solution has been the subject of further study, and the reaction resulting in the replacement of the first hydrogen atom is found to be pseudo-unimolecular with a high temperature coefficient.[30] Complete interchange between deuterium and the hydrogen in the NH_3 groups of metal ammines occurs when the latter are dissolved in water containing deuterium oxide.[31] Atomic deuterium enters into exchange reactions with water vapour, ammonia, and acetylene, but not with methane,[32] contrary to results previously reported.[33] Catalytic exchange reactions between D_2 and H_2O and between H_2 and D_2O on the surfaces of chromium sesquioxide, zinc oxide and chromite, alumina and platinised asbestos have been observed : the variation of the former reaction velocity with temperature on the first catalyst has been determined approximately and the mechanism has been discussed.[34] Methane exchanges [35] with deuterium on a nickel catalyst at 184—305°, and ammonia similarly reacts with deuterium on a $Fe–Al_2O_3–K_2O$ catalyst at room temperature; [36] the bearing of the latter observation on the kinetics of the ammonia synthesis is discussed. Benzene and deuterium oxide exchange readily at 200° on nickel–kieselguhr, the product consisting of an equilibrium mixture of various deuterobenzenes [37] (see also p. 48). A serious source of error in exchange experiments has been indicated as being caused by hydrogen remaining adsorbed on quartz vessels and platinum wires even when apparently thoroughly out-gassed.[38]

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[21] O. Reitz and K. F. Bonhoeffer, *Z. physikal. Chem.*, 1935, **174**, 559.

[22] C. K. Ingold, C. G. Raisin, and C. L. Wilson, *Nature*, 1934, **134**, 734; *A.*, 1935, 74.

[23] J. Horiuti and M. Polanyi, *ibid.*, 1934, **134**, 847; *A.*, 1935, 74; C. K. Ingold, C. G. Raisin, and C. L. Wilson, *ibid.*, p. 847; *A.*, 1935, 74.

[24] P. Goldfinger and V. Lasarev, *Compt. rend.*, 1935, **200**, 1671; *A.*, 965.

[25] L. H. Reyerson, *J. Amer. Chem. Soc.*, 1935, **57**, 779; *A.*, 713; L. H. Reyerson and B. Gillespie, *ibid.*, p. 2250.

[26] R. P. Bell, *ibid.*, p. 778; *A.*, 713.

[27] H. Erlenmeyer and H. Gärtner, *loc. cit.*, ref. (19).

[28] T. Titani and M. Harada, *Bull. Chem. Soc. Japan*, 1935, **10**, 205, 261; *A.*, 944, 1212.

[29] W. H. Hamill and W. Freudenberg, *J. Amer. Chem. Soc.*, 1935, **57**, 1427; *A.*, 1212.

[30] J. O. Halford, L. C. Anderson, J. R. Bates, and R. D. Swisher, *ibid.*, p. 1663.

Properties. The melting points of hydrogen and deuterium have been determined as 13·95° and 18·59° Abs., respectively, and the corresponding heats of fusion are 28·0 and 47·0 g.-cals. The characteristic (Debye) temperatures, for C_p, of the solids are 91° and 89°, respectively.[39] The heats of evaporation [40] of liquid hydrogen and deuterium at 19·65° Abs., and the vapour pressures of *o*- and *p*-deuterium at 20·38° Abs., of *o*- and *p*-hydrogen at 17·13° Abs.,[41] and of *n*- and *e*-deuterium over the range 15—20·4° Abs.[42] have been measured. Differences in the properties of hydrogen and deuterium are attributed partly to differences in zero-point energies and partly to other factors.[40] The heat capacities [43] of *o*- and *n*-deuterium have been determined and the entropy of *n*-deuterium at 298·1° Abs. evaluated : [44] the result is compared with that calculated from spectroscopic data by the statistical method, and the difference in the two values explained by the persistence of rotation in the solid state (cf. p. 88). The thermal conductivity,[45] volume coefficient of expansion,[46] molecular diameter,[47] viscosity,[47a] and rates of diffusion of deuterium gas through palladium [48] and copper [49] have been studied, and the results compared with those for hydrogen gas. The difference in adsorption of hydrogen and deuterium on various surfaces has been investigated from both theoretical [50] and practical standpoints ; [51] one of the applications of the latter is in connexion with the reaction with ethylene.[52] The ratio of the magnetic moment of the proton to that of the deuteron has been determined at 83°, 193°, and 293° Abs. by the method based on the rates of the paramagnetic ortho-para conversion of hydrogen and deuterium.[53] Provisional mass-spectrographic values for the atomic weights of the two isotopes, based on O^{16}, have been published ; accurate results are desirable, as they may help in the estimation of the deuterium oxide content of normal water.[54]

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[31] H. Erlenmeyer and H. Gärtner, *Helv. Chim. Acta*, 1934, **17**, 1008; *A.*, 1934, 1321; H. Erlenmeyer and H. Lobeck, *ibid.*, 1935, **18**, 1213; *A.*, 1332.

[32] K. H. Geib and E. W. R. Steacie, *Z. physikal. Chem.*, 1935, **29**, [*B*], 215; *A.*, 1087.

[33] H. S. Taylor, K. Morikawa, and W. S. Benedict, *J. Amer. Chem. Soc.*, 1935, **57**, 383; *A.*, 457.

[34] H. S. Taylor and H. Diamond, *ibid.*, p. 1256; *A.*, 1085.

[35] H. S. Taylor *et al.*, *loc. cit.*, ref. (33).

[36] H. S. Taylor and J. C. Jungers, *ibid.*, p. 660; *A.*, 710; see also K. Wirtz, *Z. physikal. Chem.*, 1935, [*B*], **30**, 289.

[37] P. I. Bowman, W. S. Benedict, and H. S. Taylor, *J. Amer. Chem. Soc.*, 1935, **57**, 960; *A.*, 852.

[38] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1935, **31**, 821; *A.*, 710.

[39] K. Clusius and E. Bartholomé, *Physikal. Z.*, 1934, **35**, 969; *A.*, 1935, 155.

[40] *Idem*, *Z. physikal. Chem.*, 1935, [*B*], **30**, 237.

[41] K. Clusius, *ibid.*, 1935, [*B*], **29**, 159; *A.*, 925.

[42] F. G. Brickwedde ,R. B. Scott, and H. S. Taylor, *J. Chem. Physics*, 1935, **3**, 653.

Deuterium oxide. The value of $d^{20^\circ}_{20^\circ}$ for pure deuterium oxide is now reported [55] as 1·1071, which is lower than that previously accepted,[56] the difference being probably due to the larger O^{18} content : for water containing less than 1 part of deuterium oxide in 2×10^5, $d_{20^\circ}^{20^\circ}$ is 0·9999815. Measurements have been made of the heat capacities [57] of liquid and solid deuterium oxide, of the heats of fusion [57, 58] and melting points of mixtures [59] of light and heavy ice, of the heats of vaporisation and dilution,[60] and of the vapour pressures [61] of mixtures of liquid water and deuterium oxide. The general P–V–T relationships of solid and liquid deuterium oxide have been studied,[62] and different forms of heavy ice identified. The differences in the thermal properties of water and deuterium oxide cannot be accounted for by their zero-point energies only; the importance of angular vibration or " libration " of the molecules has also been considered.[63] Observations have also been described of the refractive index,[64] dielectric constant,[65] surface tension,[66] and critical temperature [67] of liquid deuterium oxide, of its diffusion in ordinary water,[68] of the diamagnetism [69] of the liquid and solid states, and of the cell-dimensions [70] of solid deuterium oxide.

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[43] K. Clusius and E. Bartholomé, *Nach. Ges. Wiss. Göttingen, Math.-phys. Kl.*, 1934, [ii], **1**, 1 ; *Z. physikal. Chem.*, 1935, [*B*], **29**, 162 ; *A.*, 573, 924.

[44] *Idem, ibid.*, 1935, [*B*], **30**, 237.

[45] A. B. van Cleave and O. Maass, *Canadian J. Res.*, 1935, **12**, 372 ; *A.*, 691.

[46] J. B. M. Coppock, *Trans. Faraday Soc.*, 1935, **31**, 913 ; *A.*, 1064.

[47] A. B. van Cleave and O. Maass, *Canadian J. Res.*, 1935, **12**, 57 ; *A.*, 432.

[47a] I. Amdur, *J. Amer. Chem. Soc.*, 1935, **57**, 588.

[48] W. Jost and A. Widmann, *Z. physikal. Chem.*, 1935, [*B*], **29**, 247 ; *A.*, 1200 ; H. W. Melville and E. K. Rideal, *Proc. Roy. Soc.*, 1935, [*A*], **153**, 89 ; O. Luhr and L. Harris, *loc. cit.*, ref. (16) ; see also A. Sieverts and G. Zapf, *Z. physikal. Chem.*, 1935, **174**, 559.

[49] H. W. Melville and E. K. Rideal, *loc. cit.*, ref. (48).

[50] J. E. Lennard-Jones and C. Strachan, *Proc. Roy. Soc.*, 1935, [*A*], **150**, 442, 456 ; *A.*, 1070.

[51] J. Pace and H. S. Taylor, *J. Chem. Physics*, 1934, **2**, 578 ; *A.*, 1934, 1181 ; R. Klar, *Naturwiss.*, 1934, **22**, 822 ; *A.*, 1935, 27 ; H. W. Kohlschütter, *Z. physikal. Chem.*, 1934, **170**, 300 ; *A.*, 1935, 27 ; R. Klar, *ibid.*, 1935, **174**, 1 ; *A.*, 1329 ; H. W. Melville and E. K. Rideal, *Proc. Roy. Soc.*, 1935, [*A*], **153**, 77.

[52] R. Klar, *loc. cit.* ; *Z. physikal. Chem.*, 1934, [*B*], **27**, 319 ; *A.*, 1935, 175.

[53] L. Farkas and A. Farkas, *Nature*, 1935, **135**, 372 ; *A.*, 560.

[54] F. W. Aston, *ibid.*, 1935, **135**, 541 ; *A.*, 677.

[55] L. Tronstad, J. Nordhagen, and J. Brun, *ibid.*, 1935, **136**, 515 ; *A.*, 1313.

The ratio of the dissociation constants [71] of deuterium oxide and water is said to be 0·16 to 1 at 21°, from measurements with cells involving deuterium electrodes in deuterium chloride and sodium deuteroxide solutions. The dipole moment of the deuterium oxide molecule, measured either in the vapour state [72] or in solution in benzene [73] or dioxan,[65] is not more than 0·02 × 10^{-18} e.s.u. greater than for water, although a somewhat larger difference might have been expected theoretically.[74] A similar difference of 0·03 × 10^{-18} e.s.u. exists between the dipole moments of ammonia and trideuterammonia.[75] Freezing-point determinations of solutions of water and of deuterium oxide in dioxan indicate that the latter is slightly more associated in this solvent,[76] and a similar conclusion is derived from the difference in the heat capacities of the liquids.[77] Replacement of H_2O by D_2O in binary systems with organic compounds, *e.g.*, phenol, acetonitrile, triethylamine, and propionic acid, raises the upper and depresses the lower consolute temperatures.[78]

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[56] H. S. Taylor and P. W. Selwood, *J. Amer. Chem. Soc.*, 1934, **56**, 998; *A.*, 1934, 590; see also, *ibid.*, 1935, **57**, 642, footnote (4).

[57] R. S. Brown, W. H. Barnes, and O. Maass, *Canadian J. Res.*, 1935, **12**, 699; *A.*, 1198; E. Bartholomé and K. Clusius, *Z. physikal. Chem.*, 1935, [*B*], **28**, 167; *A.*, 584.

[58] L. Jacobs, *Trans. Faraday Soc.*, 1935, **31**, 813; *A.*, 704.

[59] V. K. LaMer and W. N. Baker, *J. Amer. Chem. Soc.*, 1934, **56**, 2641; *A.*, 1935, 167.

[60] E. Doehlemann and E. Lange, *Z. physikal. Chem.*, 1935, **173**, 295; *A.*, 935.

[61] W. F. K. Wynne-Jones, *J. Chem. Physics*, 1935, **3**, 197; *A.*, 694; M. H. Wahl and H. C. Urey, *loc. cit.*, ref. (14).

[62] G. Tammann and G. Bandel, *Z. anorg. Chem.*, 1935, **221**, 391; *A.*, 302; J. Timmermans and L. Deffet, *Compt. rend.*, 1935, **200**, 1661; *A.*, 815; P. W. Bridgman, *J. Chem. Physics*, 1935, **3**, 597; *A.*, 1454.

[63] J. D. Bernal and G. Tamm, *Nature*, 1935, **135**, 229; *A.*, 432; P. W. Bridgman, *loc. cit.*, ref. (62).

[64] W. J. C. Orr, *ibid.*, p. 793; *A.*, 810.

[65] P. Abadie and G. Champetier, *Compt. rend.*, 1935, **200**, 1590; *A.*, 808.

[66] I. Minkow, *Nature*, 1935, **136**, 186; *A.*, 1059.

[67] E. H. Riesenfeld and T. L. Chang, *Z. physikal. Chem.*, 1935, [*B*], **28**, 408; **30**, 61; *A.*, 691.

[68] W. J. C. Orr and D. W. Thomson, *Nature*, 1934, **134**, 776; *A.*, 1935, 25; M. Temkin, *ibid.*, 1935, **136**, 552; *A.*, 1313; W. J. C. Orr and J. A. V. Butler, *J.*, 1935, 1273; *A.*, 1313.

[69] F. W. Gray and J. H. Cruickshank, *Nature*, 1935, **135**, 268; *A.*, 435; B. Cabrera and H. Fahlenbrach, *Anal. Fis. Quim.*, 1934, **32**, 538; *A.*, 1935, 923.

[70] H. D. Megaw, *Nature*, 1934, **134**, 900; *A.*, 1935, 151.

[71] E. Abel, E. Bratu, and O. Redlich, *Z. physikal. Chem.*, 1935, **173**, 353; cf. *Ann. Reports*, 1934, **31**, 17.

Deuterium compounds. The absorption spectra of the bromides [79] and iodides [80] of hydrogen and deuterium have been studied, and the reason for the differences considered. The vapour pressures and boiling points [79] (206·3° Abs.) of the two bromides are identical, but the vapour pressure of deuterium iodide [80] is slightly greater than that of hydrogen iodide, and the boiling point of the former (237·0° Abs.) is consequently 0·5° lower. The higher vapour pressure of the deuterium compound is probably due to factors different from those which result in its fluoride having a higher vapour pressure than that of hydrogen. According to an approximate theoretical treatment,[81] the vapour-pressure curves of the corresponding hydrogen and deuterium compounds should cross at some temperature: this is apparently often above the boiling point, and so the conditions under which the latter have the higher vapour pressure are not often observable. The transition point of sodium sulphate decadeuterate ($Na_2SO_4,10D_2O$) is 34·48°.[82]

Pure hexadeuterobenzene [83] has been obtained by distilling the calcium salt of mellitic acid with calcium deuteroxide and also by applying the Friedel–Crafts reaction to benzene and deuterium chloride: it has f. p. + 6·8° and b. p. 79·4°, the corresponding values for benzene being + 5·5° and + 80·12°. These results agree with some previously published,[84] but differ markedly from others in which the hexadeuterobenzene was made by passing dideuteracetylene over a tellurium catalyst.[85] Octadeuteronaphthalene is said to be obtained as a by-product in the latter process.[86] The exchange between benzene and deuterium oxide on a nickel–kieselguhr catalyst, already mentioned (p. 44), has been used to prepare hexadeuterobenzene; if the mixed benzenes are separated after equilibrium is attained, and re-heated with pure deuterium oxide, it is claimed that hexadeuterobenzene of over 99% purity, $d_{4^\circ}^{25^\circ}$ 0·9417, can be obtained after four operations.[37] Dideuteromalonic deuteracid, $CD_2(CO_2D)_2$, results from the action of deuterium oxide on carbon suboxide; on heating to 140—150°, trideuteracetic deuteracid, $CD_3 \cdot CO_2D$, m. p. 15·75°, is obtained. The latter substance is more volatile than acetic acid.[87] Catalytic reduction of linoleic acid with deuterium yields 6 : 7 : 9 : 10-tetradeuterostearic acid,[88] and the addition of deuterium to cholestenone gives 4 : 5-dideuterocoprostanone,[89] which has been used as an " indicator " in biological experiments.

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[72] L. G. Groves and S. Sugden, *J.*, 1935, 971.

[73] F. H. Müller, *Physikal. Z.*, 1934, **35**, 1009; *A.*, 1935, 148.

[74] R. P. Bell, *Trans. Faraday Soc.*, 1935, **31**, 1345; *A.*, 1304.

[75] J. M. A. de Bruyne and C. P. Smyth, *J. Amer. Chem. Soc.*, 1935, **57**, 1203; *A.*, 1055.

[76] R. P. Bell and J. H. Wolfenden, *J.*, 1935, 822; *A.*, 931.

[77] R. S. Brown, W. H. Barnes, and O. Maass, *loc. cit.*, ref. (57).

[78] J. Timmermans and G. Poppe, *Compt. rend.*, 1935, **201**, 524; *A.*, 1314.

[79] J. R. Bates, J. O. Halford, and L. C. Anderson, *J. Chem. Physics*, 1935, **3**, 531; *A.*, 1313.

[80] *Idem, ibid.*, p. 415; *A.*, 1064.

[81] H. C. Urey and G. K. Teal, *loc. cit.*, ref. (4), p. 58.

[82] H. S. Taylor, *J. Amer. Chem. Soc.*, 1934, **56**, 2643; *A.*, 1935, 447.

[83] H. Erlenmeyer and H. Lobeck, *Helv. Chim. Acta*, 1935, **18**, 1464; A. Klit and A. Langseth, *Nature*, 1935, **135**, 956; *A.*, 806.

Solutions in heavy water. The conductivities[90] of potassium chloride and of deuterium chloride in deuterium oxide are 17% and 26%, respectively, less than the corresponding values in water; the differences are chiefly due to a 23% increase in the viscosity of the solvent. Similar decreases in the conductivities of hydrochloric and perchloric acids in deuterium oxide solution have been noted.[91] The conductances of mixtures of the chlorides of hydrogen and deuterium are less than the expected values : the discrepancy can be explained by supposing that hydrogen and deuterium ions take part in Grotthuss conduction.[90] The ratio of the dissociation constants of a weak acid in water and in deuterium oxide should be larger the weaker the acid.[92] The free energy of hydration of the hydrogen ion is stated to be greater in deuterium oxide than in water; a similar difference is supposed to exist for hydrogen- and deutero-acids.[93] The potential of the quinhydrone electrode in $0{\cdot}001M$-hydrochloric acid in deuterium oxide has been found to be 0·0345 volt more positive than in water; the ratio of the products of the two dissociation constants in water to that in deuterium oxide is 3·84.[94] The cathodic overvoltage at mercury is greater for the liberation of deuterium than of hydrogen, as is to be expected; the temperature coefficient is greater for the former.[95] Observations have also been made with the dropping-mercury cathode in various solutions containing deuterium oxide.[96]

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[84] C. L. Wilson, *Nature*, 1935, **136**, 301; *A.*, 1198.

[85] G. R. Clemo and A. McQuillen, *J.*, 1935, 881; *A.*, 967.

[86] *Idem, ibid.*, p. 1325; *A.*, 1358.

[87] C. L. Wilson, *ibid.*, p. 492; *A.*, 731.

[88] R. Schönheimer and D. Rittenberg, *J. Biol. Chem.*, 1935, **111**, 163; *A.*, 1407.

[89] R. Schönheimer, D. Rittenberg, and M. Graff, *ibid.*, p. 183; *A.*, 1407.

[90] W. N. Baker and V. K. LaMer, *J. Chem. Physics*, 1935, **3**, 406; *A.*, 1078.

[91] A. Fink, P. Gross, and H. Steiner, *Monatsh.*, 1935, **66**, 111; *A.*, 1324.

[92] O. Halpern, *J. Chem. Physics*, 1935, **3**, 456; *A.*, 1203.

Kinetics, etc. The spectroscopy, reaction kinetics, and surface chemistry of deuterium compounds are mainly treated elsewhere in these Reports : mention may be made in addition of the following topics. Two papers [97] dealing with the application of quantum mechanics to reactions involving hydrogen and deuterium have appeared, and a review article [98] on the use of the latter in the study of acid–base catalysis has been published. The catalytic decompositions of nitroamine by hydrochloric acid [99] and of hydrogen peroxide [1] by the iodide ion are slower in deuterium oxide than in water, although for the latter reaction the energies of activation are the same for both media in spite of the differences in the zero-point energies of hydrogen peroxide and deuterium peroxide. The catalysis of H_2O and D_2 exchange by enzymes has been investigated;[2] the enzymic fission of salicin by emulsin is 25% more rapid in deuterium oxide than in water.[3] The photo-oxidation of the iodides of hydrogen and deuterium shows that the reactions between H or D and oxygen are three-body processes, and $k_{\mathrm{H+O_2+O_2}} \approx k_{\mathrm{D+O_2+O_2}}$.[4] The rate of the mercury-photosensitised decomposition of acetylene is about 30% greater than for dideuteracetylene,[5] and a similar difference is observed in the combination of oxygen with hydrogen or deuterium in the presence of α-particles.[6] The rate of polymerisation of dideuteracetylene under the influence of α-particles is, however, the same as for acetylene.[7] The decomposition of trideuterammonia, like that of ammonia, on a tungsten filament is approximately of zero order, although the former reaction is the slower.[8] A comparison has been made of the rates of ortho–para hydrogen conversion and of the $H_2 + D_2 = 2HD$ reaction on a nickel catalyst: the mechanism of both processes is evidently the same.[9]

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[93] P. Goldfinger and W. Jeunehomme, *Compt. rend.*, 1935, **200**, 1387; *A.*, 824.

[94] V. K. LaMer and S. Korman, *J. Amer. Chem. Soc.*, 1935, **57**, 1511; *A.*, 1205.

[95] F. P. Bowden and H. F. Kenyon, *Nature*, 1935, **135**, 105; *A.*, 450.

[96] J. Heyrovský and O. H. Müller, *Coll. Czech. Chem. Comm.*, 1935, **7**, 281; *A.*, 1079; O. H. Müller, *ibid.*, p. 321; *A.*, 1208.

[97] R. A. Smith, *Proc. Camb. Phil. Soc.*, 1934, **30**, 508; *A.*, 1935, 306; R. P. Bell, *Proc. Roy. Soc.*, 1935, [*A*], **148**, 241; *A.*, 560.

[98] W. F. K. Wynne-Jones, *Chem. Reviews*, 1935, **17**, 115.

[99] C. A. Marlies and V. K. LaMer, *J. Amer. Chem. Soc.*, 1935, **57**, 1812; *A.*, 1466.

[1] E. Abel, O. Redlich, and W. Stricks, *Monatsh.*, 1935, **65**, 380; *A.*, 939.

[2] G. H. Bottomley, B. Cavanagh, and M. Polanyi, *Nature*, 1935, **136**, 103; *A.*, 1084.

[3] E. W. R. Steacie, *Z. physikal. Chem.*, 1935, [*B*], **28**, 236; *A.*, 588.

[4] G. A. Cook and J. R. Bates, *J. Amer. Chem. Soc.*, 1935, **57**, 1775.

[5] J. C. Jungers and H. S. Taylor, *J. Chem. Physics*, 1935, **3**, 338; *A.*, 943.

Other Isotopes.—Tritium. Graphical arrangements of the known isotopes of elements of low atomic weight indicated the possibility of the existence of an isotope of hydrogen of mass 3, now called "tritium" and given the symbol T. It was claimed [10] that the presence of tritium oxide in water containing 2% of deuterium oxide could be detected by the magneto-optic method, but band-spectroscopic examination [11] showed that the upper limit of its concentration was 6 parts in 10^6 of ordinary hydrogen; by the aid of the mass-spectrograph [12] this limit was placed at 2 parts in 10^9 as a maximum. Working with 99% deuterium oxide, G. Hertz has definitely proved the presence of tritium by its mass-spectrogram; [13] the T : D ratio was 5 : 10^6, indicating a proportion of 1 part, or less, of tritium in 10^9 of natural hydrogen. Study of the impacts of high-speed deuterons on deuterium nuclei had indicated the occurrence of the disintegration [14] $D + D \longrightarrow H + T$, and the passage of a positive-ray discharge through deuterium is stated [15] to result in an increase of the T/D ratio from 1/200,000 to 1/5000: the absolute amount of tritium formed must, however, be very small. In spite of the apparent hopelessness of the task, 75 metric tons of water have been electrolysed down to 0·5 c.c.,[16] which was found to contain 1 part of tritium oxide in 4000: the abundance of tritium in ordinary water is estimated as 7 parts in 10^{10}. Under the experimental conditions, apparently nickel electrodes in alkali, the D_2–T_2 separation coefficient is 2·0, in agreement with theoretical predictions.[17] It appears probable that small quantities of water enriched with tritium will soon be available for experimental work.

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[6] S. C. Lind and C. H. Schiflett, *J. Amer. Chem. Soc.*, 1935, **57**, 1051; *A.*, 944.

[7] S. C. Lind, J. C. Jungers, and C. H. Schiflett, *ibid.*, p. 1032; *A.*, 943.

[8] J. C. Jungers and H. S. Taylor, *ibid.*, p. 679; *A.*, 710.

[9] E. Fajans, *Z. physikal. Chem.*, 1935, [*B*], **28**, 239; *A.*, 710.

[10] W. M. Latimer and H. A. Young, *Physical Rev.*, 1933, **44**, 690.

[11] G. N. Lewis and F. H. Spedding, *ibid.*, 1933, **43**, 964.

[12] W. Bleakney and A. J. Gould, *ibid.*, 1934, **45**, 281.

[13] W. W. Lozier, P. T. Smith, and W. Bleakney, *ibid.*, p. 655; M. A. Tuve, L. R. Hafstad, and O. Dahl, *ibid.*, pp. 746, 840.

[14] *Ann. Reports*, 1934, **31**, 387.

[15] G. P. Harnwell, H. D. Smyth, S. N. van Voorhis, and J. B. H. Kuper, *Physical Rev.*, 1934, **45**, 655.

[16] P. W. Selwood, H. S. Taylor, W. W. Lozier, and W. Bleakney, *J. Amer. Chem. Soc.*, 1935, **57**, 780; *A.*, 711.

Oxygen and Nitrogen Isotopes.—Water containing O^{18} in excess of the normal has been obtained by a diffusion method,[18] and a slight enrichment has been observed in oxygen obtained from liquid air by the fractionation process;[19] the difference[20] of 1·4% in the vapour pressures of H_2O^{16} and H_2O^{18} has resulted in a partial separation by the fractional distillation of water.[21] Decomposition of 30% hydrogen peroxide by colloidal platinum yields a gas with a O^{16}/O^{18} ratio of 462 ± 8, compared with 426 ± 4 for the residue.[22] Conflicting reports on the efficiency of electrolysis in bringing about a concentration of O^{18} have been published: in early work no enrichment was observed,[23] but the reason for this is now apparent (see below). More recently the concentration of O^{18} in the residual water has been established,[24] although the separation factor appears generally to be no more than 1·01 : the reduction of the volume of water 100,000-fold by electrolysis increases the O^{18} content of ordinary oxygen from 0·20 to only 0·22%.[25] A separation coefficient of 1·15 has been reported recently[26] for the electrolysis of 1·25N-sodium hydroxide with nickel electrodes, although a previous claim[27] for a coefficient of the same order has now been revised[28] to 1·05. Assuming the rate-determining step in the separation of O_2 by electrolysis is the passage of a $O^{18}H$ or $O^{16}H$ complex over or through an energy barrier, a separation coefficient of 1—1·16 can be calculated,[26] according to the width and height of the barrier. The most favourable value would lead only to a four-fold increase in concentration of O^{18}, whilst the deuterium concentration in water was raised from 1 in 5000 to 100%. Such an enrichment would provide a tool of value to chemists, but it is doubtful if even this relatively low efficiency could be attained, especially as an alternative, approximate, calculation indicates a probable factor of 1·06 for the ratio of the rates of separation of O_2^{16} and O_2^{18} on electrolysis.[25] Calculations by statistical methods [29] (p. 70) of the equilibrium constant of the exchange reaction $2H_2O^{18}\ (l) + O_2^{16} = 2H_2O^{16}\ (l) + O_2^{18}$ gives a value of 1·012, implying an enrichment factor of 1·006 at 25° : this equilibrium, which opposes the normal electrolytic separation, will tend to be attained in the evolution of oxygen, and may explain the different electrolytic separation coefficients reported by different workers.[25] The equilibrium constant of the reaction $2H_2O^{18}\ (l) + CO_2^{16} = 2H_2O^{16}\ (l) + CO_2^{18}$ has been calculated,[29] and the result shows that the carbon dioxide gas should always contain a larger proportion of O^{18} than does the water : the theoretical fractionation factor, *i.e.*, the ratio O^{18}/O^{16} in the gas to that in the water, of 1·047 at 0° has been confirmed experimentally.[30] A counter-current process, based on the establishment of the equilibrium, for obtaining carbon dioxide enriched with O^{18}, has been devised [29] and is being tested. It is the use of carbon dioxide for the neutralisation of the alkali that had become concentrated on electrolysis, which was probably responsible for the failure to detect any change of O^{18} in the early work mentioned above.[82, 25]

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[17] H. Eyring, quoted in ref. (16).

[18] *Z. Physik*, 1932, **79**, 108; see M. Polanyi and A. S. Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508; *A.*, 1934, 979.

[19] R. Klar and A. Krauss, *Naturwiss.*, 1934, **22**, 119; *A.*, 1934, 377; E. R. Smith, *J. Chem. Physics*, 1934, **2**, 298; *A.*, 1934, 855.

[20] M. H. Wahl and H. C. Urey, *ibid.*, 1935, **3**, 411.

[21] G. N. Lewis and R. E. Cornish, *J. Amer. Chem. Soc.*, 1933, **55**, 2616; G. N. Lewis, *ibid.*, p. 3502.

[22] H. S. Taylor and A. J. Gould, *ibid.*, 1934, **56**, 1823; *A.*, 1934, 1082.

[23] G. N. Lewis and R. T. Macdonald, *J. Chem. Physics*, 1933, **1**, 341; *A.*, 1934, 10; P. W. Selwood and A. A. Frost, *J. Amer. Chem. Soc.*, 1933, **55**, 4335; *A.*, 1933, 1233; W. Bleakney and A. J. Gould, *loc. cit.*, ref. (12).

[24] E. W. Washburn, E. R. Smith, and M. Frandsen, *J. Res. Nat. Bur. Stand.*, 1933, **11**, 453; *A.*, 1934, 156; E. W. Washburn, E. R. Smith, and F. A. Smith, *ibid.*, 1934, **13**, 599; *A.*, 1935, 175; C. H. Greene and R. J. Voskuyl, *J. Amer. Chem. Soc.*, 1934, **56**, 1649; H. L. Johnston, *ibid.*, 1935, **57**, 484; *A.*, 590; W. H. Hall and H. L. Johnston, *ibid.*, p. 1515; *A.*, 1330.

[25] P. W. Selwood, H. S. Taylor, J. A. Hipple, and W. Bleakney, *ibid.*, p. 642; *A.*, 711.

[26] G. Ogden, *Nature*, 1935, **136**, 912.

[27] E. W. Washburn, E. R. Smith, and F. A. Smith, *loc. cit.*, ref. (24).

[28] E. R. Smith and M. Wojciechowski, *J. Res. Nat. Bur. Stand.*, 1935, **15**, 187; *A.*, 1329.

An attempt has been made to concentrate N^{15} by the fractional distillation of liquid ammonia : the results so far are not very encouraging, but they indicate that the method may be of some use for increasing the N^{15}/N^{14} ratio.[31]

Artificially-radioactive Isotopes.—Mention may be made of the use of these substances as indicators in chemical investigations. By taking advantage of the radioactivity induced in bromine by neutron bombardment, it has been shown that the bromide ion in sodium bromide undergoes exchange with elementary bromine in aqueous solution.[32] Iodine and sodium iodide exchange readily in a similar manner, as also does iodine with methyl and allyl iodides; ethyl, *n*-propyl, *iso*propyl, and methylene iodides and iodoform, however, exchange very slowly, if at all.[33] Only the iodide ion of diphenyliodonium iodide undergoes exchange with iodine; the experimental results are used to throw light on the mechanism of the decomposition of the iodide in iodobenzene solution.[34] The rate of exchange of elementary iodine with the iodine in *sec.*-octyl iodide is equal to the rate of racemisation of the *d*-iodide : [35] the significance of this result is discussed elsewhere in these Reports (p. 96). A start has also been made in what is likely to be an important development, namely, the use of the radioactive isotope P^{32} in the study of metabolic processes.[36]

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[29] H. C. Urey and L. J. Greiff, *J. Amer. Chem. Soc.*, 1935, **57**, 321; *A.*, 446.

[30] L. A. Webster, M. H. Wahl, and H. C. Urey, *J. Chem. Physics*, 1935, **3**, 129; *A.*, 593; see also M. P. Applebey and G. Ogden, *J.*, 1936, 163.

[31] M. H. Wahl, J. F. Huffman, and J. A. Hipple, *J. Chem. Physics*, 1935, **3**, 434.

[32] A. von Grosse and M. S. Agruss, *J. Amer. Chem. Soc.*, 1935, **57**, 591; *A.*, 595.

S. G.

3. SPECTROSCOPY.

Atomic Spectra and the Spectra of Diatomic Molecules.—In neither of these fields are there any striking advances to report. This is to be expected, since the fundamental and important steps in each were made several years ago, and all that remains is to fill in the gaps in our knowledge of the energy levels of the less common atoms and molecules. The results for atomic states have been tabulated in a book by R. F. Bacher and S. Goudsmit.[1] Recently, interest has shifted towards the determination of nuclear magnetic moments from the investigation of the hyperfine structure of spectral lines. This has already been dealt with in last year's Reports [2] and need not be repeated here, especially since it is only of secondary interest to chemists. The corresponding collection of results regarding the energy levels and electronic structure of diatomic molecules has just appeared in an excellent compilation by Frl. H. Sponer (see p. 39). For more general treatment, reference should be made to earlier Reports [3] or to the books of R. de L. Kronig [4] and of W. Jevons [5] and to the reports of R. S. Mulliken.[6]

Spectra of Polyatomic Molecules.—It is here that the most interesting advances have been made from the chemical standpoint. Instead of giving detailed results, it would appear more valuable, however, to take stock of what has been done during the past few years, reviewing the principles and methods by which it has been accomplished,[7] in order that limitations on future progress may be clearly realised. The polyatomic molecule may best be approached by considering what it has in common with, and wherein it differs from, the diatomic molecule. Just as the energy of a diatomic molecule may be divided into three (practically independent) parts, *viz.*, electronic, vibrational, and rotational, so may that of a polyatomic molecule, and consequently the latter has three distinct spectra : a pure rotation, a vibration–rotation, and an electronic spectrum. The differences between a diatomic and a polyatomic molecule become evident as soon as we consider the structure of any one of these three types. This follows since the expression for the energy of a polyatomic molecule is considerably more complicated than that for a diatomic molecule, as well as the selection rules governing its allowed changes. For example, a diatomic molecule has effectively only one moment of inertia, whereas the general polyatomic molecule has three different moments of inertia; the expression for the rotational energy in the first case is consequently very simple, while in the second case no explicit expression exists for the energy levels, although these can be computed. Again, the diatomic molecule has only one degree of vibrational freedom, or one fundamental vibration frequency, whereas the polyatomic molecule of n atoms has, in general, $3n - 6$ fundamental frequencies with a set of selection rules governing the appearance of each in the different types of spectra. Finally, the electronic energy states of a diatomic molecule are usually characterised by the associated resultant angular momentum about the internuclear axis, whereas in a polyatomic molecule these have to be specified through the symmetry and transformation properties of the associated wave functions. Nevertheless, the apparently hopeless complexity which such factors introduce into the spectra of polyatomic molecules has proved to be more capable of disentanglement than one would have at first supposed.

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[33] F. Juliusburger, B. Topley, and J. Weiss, *J. Chem. Physics*, 1935, **3**, 437.

[34] *Idem, J.*, 1935, 1295.

[35] E. D. Hughes, F. Juliusburger, S. Masterman, B. Topley, and J. Weiss, *ibid.*, p. 1525.

[36] O. Chiewitz and G. von Hevesy, *Nature*, 1935, **136**, 754.

[1] " Atomic Energy States," McGraw-Hill, 1933.

[2] *Ann. Reports*, 1934, **31**, 372.

[3] *Ibid.*, 1933, **30**, 68.

[4] " The Optical Basis of the Theory of Valency," Cambridge, 1935; " Band Spectra and Molecular Structure," Cambridge, 1930.

[5] " Report on the Spectra of Diatomic Molecules," Cambridge, 1932.

[6] *Rev. Mod. Physics*, 1930, **2**, 60; 1931, **3**, 89; 1932, **4**, 1.

Before passing to the consideration of the three main classes of spectra, it should be mentioned that these are all normally observed in absorption. In the case of the first two, however, they may also be obtained by scattering (Raman spectra),[8] although the selection rules differ from those operative in absorption, and we shall have to consider the relation between them more fully in what follows.

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[7] D. M. Dennison, *Rev. Mod. Physics*, 1931, **3**, 280. Articles by R. Mecke, E. Teller, and O. Reinkober in the "Hand- und Jahrbuch der Chemischen Physik," 1934, Band 9/11; G. B. B. M. Sutherland, "Infra-Red and Raman Spectra," Methuen, 1935.

[8] *Ann. Reports*, **1934**, **31**, 21.

A. *Pure rotation spectra.* For convenience in this and other sections, we shall immediately divide polyatomic molecules into four classes according to their degree of rotational symmetry. If the three moments of inertia are denoted by I_A, I_B, I_C, then there are four classes of molecules: (1) *linear molecules,* for which $I_A = I_B, I_C = 0$; (2) *spherical molecules,* for which $I_A = I_B = I_C$; (3) *symmetrical top molecules,* for which $I_A = I_B \neq I_C$; and (4) *asymmetrical top molecules,* for which $I_A \neq I_B \neq I_C$. The corresponding energy expressions and selection rules have been collected in Table I. By examination of this table and application of the appropriate selection rule, it is clear that the pure rotation spectrum of a linear polyatomic molecule is in no way different from that of a diatomic molecule. Next, we note that spherically symmetrical molecules (such as methane, carbon tetrachloride, etc.) have no pure rotation spectra. The absorption spectrum of a symmetrical top molecule is exactly like that of a diatomic molecule with a moment of inertia equal to that of the symmetrical top molecule perpendicular to its axis of symmetry. Thus, the spacing of the lines in the pure rotation spectrum of a symmetrical top molecule can yield no information regarding the moment of inertia about the symmetry axis (for $\Delta K = 0$ in the Raman spectrum too). The Raman spectrum is slightly more complicated, containing an O and an S branch in addition to the usual P, Q, and R ones. Although the

TABLE I.

Rotational Energy Formulæ and Selection Rules for the Four Classes of Polyatomic Molecules.

		Selection rules.	
Class of molecule.	Expression for rotational energy, E_r.	(a) Infra-red spectra.	(b) Raman spectra.
Linear $I_A = I_B$; $I_C = 0$	$\frac{h^2}{8\pi^2 I_A} J(J+1)$ $J = 0, 1, 2, \ldots$	$\Delta J = \pm 1$	$\Delta J = 0, \pm 2$
Spherical $I_A = I_B = I_C$	$\frac{h^2}{8\pi^2 I_A} J(J+1)$ $J = 0, 1, 2, \ldots$	No active transitions	No active transitions
Symmetrical top $I_A = I_B \neq I_C$	$\frac{h^2}{8\pi^2 I_A} J(J+1) + \left(\frac{1}{I_C} - \frac{1}{I_A}\right)\frac{K^2 h^2}{8\pi^2}$ $K \leqslant J$; $J = 0, 1, \ldots$	$\Delta J = \pm 1$ $\Delta K = 0$	$\Delta J = 0, \pm 1, \pm 2$ $\Delta K = 0$
Asymmetrical top $I_A \neq I_B \neq I_C$	No simple explicit expression in terms of J, the quantum number for total angular momentum.	$\Delta J = \pm 1$	$\Delta J = 0, \pm 1, \pm 2$

spacing of the lines is independent of I_O, the intensity of the lines is a function of I_O/I_A, and it is interesting to note that it has been possible in this way to confirm the flat pyramidal model of the ammonia molecule by a careful intensity measurement of its pure rotation Raman spectrum.[9]

The asymmetrical top molecule presents serious difficulties. The energy levels are characterised by the quantum number J of the total angular momentum. Corresponding to each value of J (1, 2, 3 . . .) there are $2J + 1$ sub-levels, the values of which may be computed by solving certain algebraic equations. As some of these equations will only admit of numerical (approximate) solution, it means that the moment of inertia must be known in order to make the computation. Usually a fair approximation to the values of the moments can be made from other evidence : the levels may then be computed and the agreement with observation tested. By a process of successive approximation, one finally arrives at values for the moment which give agreement with experiment. Such a procedure is extremely laborious and requires very accurate experimental data before it can be applied. In fact, no asymmetrical top molecule has had its pure rotation spectrum analysed in this idealised way, although for the H_2O molecule R. Mecke has shown that all of the known lines may be classified by treating the asymmetrical rotator as an imperfect symmetrical rotator.[10]

When one considers the experimental difficulties in obtaining this type of spectrum (under high resolution), it does not seem probable that it will ever become an important source of information for the structure of molecules. All of the information derivable can be obtained from vibration rotation or from electronic spectra, both of which are very much easier to observe. The only advantage of pure rotation spectra is their comparative simplicity, but as spectroscopists become more experienced this will not count for very much, since the degree of resolution of lines obtainable in the near infra-red and the visible region is at present as high as or higher than that obtainable at longer wave-lengths.

B. *Vibration–rotation spectra.* This is the class of spectra which has so far proved most productive of information about polyatomic molecules. Such spectra are not so complex as electronic, and yet yield just as much information as the latter do regarding the ground state of the molecule. Their investigation is almost a necessary preliminary to the study of electronic spectra, and certainly an invaluable concomitant. From their analysis, we can obtain the values of the fundamental vibration frequencies, the shape of the molecule, its moments of inertia, and (in certain cases) the internuclear distances. A detailed description of the method of analysis [7] would not be of interest here, nor would the cataloguing of results for a large number of molecules. Such information is more conveniently available elsewhere.[10a] What is important is to realise the general principles underlying these analyses, and to be able to estimate the limitations of such a method of investigating molecular structure. One is all too frequently confused by conflicting reports of the assignment of the fundamental frequencies of a molecule and of its form and moments of inertia. It is hoped that this report will give the reader some criteria which he may apply to the work on any particular molecule.

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[9] C. M. Lewis and W. V. Houston, *Physical Rev.*, 1933, **44**, 903.

[10] "Hand- und Jahrbuch der Chemischen Physik," 1934, Band 9/11.

Suppose we have given the fact that a molecule absorbs in the infra-red at wave-lengths corresponding to the frequencies ν_1, ν_2, ν_3 . . . . , and that it has Raman lines of frequency $\nu_1{}^1$, $\nu_2{}^1$, $\nu_3{}^1$; how do we set about determining any of the information just quoted? We must first establish which are the fundamental frequencies and which are the combinations and overtones of them. This is done by the application of a judicious combination of semi-empirical rules, together with strict selection rules derived from a quantum-mechanical treatment of the problem. The first of these empirical rules concerns the magnitude of the frequency. Any molecule containing a hydrogen atom may be expected to have its highest frequencies in the neighbourhood of 3500 cm.$^{-1}$. Any molecule not containing a hydrogen atom is very unlikely to have any fundamental frequency higher than 2500 cm.$^{-1}$. This enables one immediately to put an upper limit on which of the observed frequencies may, or may not, be fundamentals. Certain authors [11] have tended to carry this principle still further, and to associate definite frequencies in the molecule with definite linkages such as the C–H, O–H, C–C, C–S, etc. This is permissible only so long as it is clearly understood that it is at best a rough approximation to the truth. The C–H bond in a molecule cannot vibrate by itself and leave the rest of the molecule unaffected. The molecule *must vibrate as a whole,* although it happens that for certain of the normal modes of vibration the motion is principally confined to, and determined by, the force constants of one particular bond or group.

The next empirical criterion is that of intensity. It usually happens that the more intensely absorbed (or scattered) frequencies correspond to fundamental vibrations of the molecule. This, however, is a rule which must be applied with even more caution than the first. What exactly determines the relative intensities of fundamentals and their combinations is not yet clearly understood (for the selection rules give only those which are forbidden). It frequently happens that a fundamental is so weak as to be, to all intents and purposes, "inactive," although the selection rules give it as an "active" frequency. This is the case in water[12] and probably in ammonia and phosphine.[13] In other cases, *e.g.*, acetylene,[14] the intensity of a combination band appears to be considerably greater than that of a fundamental.

[10a] H. Sponer, "Molekulspektren," Springer, 1935.

[11] *E.g.*, K. W. F. Kohlrausch, "Der Smekal–Raman Effekt," Springer, 1931; R. Mecke, in "The Structure of Molecules," Blackie, 1931.

Another important fact is that combination frequencies are very seldom observed in the Raman spectrum. In the particular case of "resonance" with a fundamental, however, this no longer holds. Thus, in carbon dioxide[15] the overtone of the perpendicular vibration $(\underset{\downarrow}{O}\ \overset{\uparrow}{C}\ \underset{\downarrow}{O})$ happens to coincide numerically almost exactly with the symmetrical vibration $(O \longrightarrow C \longleftarrow O)$; the result is that these two energy levels lose their individuality, a certain proportion of the molecules in each vibrating in the first fashion and the remainder in the second. Thus, instead of one strong Raman line appearing corresponding to the symmetrical vibration, and an extremely weak one corresponding to the overtone of the perpendicular fundamental, we obtain two Raman frequencies of comparable intensity lying very close together. This phenomenon is probably present also in carbon tetrachloride[16] and in the methyl halides.[17]

Having made a provisional allotment of the possible fundamental frequencies, one next chooses the most likely model of the molecule, and tries to correlate the observed fundamentals with its normal modes of vibration, the latter being deduced by classical mechanics. In this, one may apply strict selection rules, for as soon as the model is chosen, and its vibrations determined, quantum mechanics yields selection rules predicting which vibrations are active in absorption, and which in Raman scattering. These rules have been derived by several authors and are now conveniently collected in several places.[7, 18] They would take too long to reproduce here. It is sufficient for our purpose to know that they depend solely on the symmetry properties of the molecules, and do not involve specific assumptions about their internal structure. We may, however, consider some of their more general aspects. The appearance of a frequency in the infra-red absorption spectrum of a molecule depends on whether there is associated with that vibration of the molecule a changing electric moment. For example, the symmetrical vibration (O ⟶ C ⟵ O) of the carbon dioxide molecule will clearly be inactive in absorption, whereas the unsymmetrical mode of vibration (O ⟶ ⟵ C O ⟶) will be expected to cause a changing electric moment and so to be active. In the Raman spectrum, on the other hand, it is the changing polarisability of the molecule which is important in determining if it will scatter light involving a particular frequency; [8] *e.g.*, in the above two frequencies of carbon dioxide, the selection rules for the Raman spectrum will be the reverse of those for the infra-red. More generally, for a molecule possessing a centre of symmetry, the same frequency can never be active both in infra-red absorption and in Raman scattering. This is of great value in assigning the fundamentals of such molecules. For molecules which have not such a high degree of symmetry, the selection rules are more concerned with the "character" of the vibration, since, as the degree of symmetry decreases, one tends to get all frequencies active both in infra-red and in Raman scattering. The "character" of a vibration means those of its properties which do not depend on the particular force field in the molecule, but rather on its geometrical or symmetry properties, *e.g.*, properties such as whether the vibration is single or degenerate; what the degree of degeneracy is in the latter case; whether the vibration is such that the change of electric moment takes place only along a particular axis of symmetry in the molecule. The last is of great importance, since the rotational fine structure of a vibration band can differ profoundly according to the direction of vibration of the associated electric moment within the molecule.

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[12] E. K. Plyler and W. W. Sleator, *Physical Rev.*, 1931, **37**, 1493; also ref. (26).

[13] J. B. Howard, *J. Chem. Physics*, 1935, **3**, 207.

[14] A. Levin and C. F. Meyer, *J. Opt. Soc. Amer.*, 1928, **16**, 137.

[15] E. Fermi, *Z. Physik*, 1931, **71**, 250; D. M. Dennison, *Physical Rev.*, 1932, **41**, 304.

[16] J. Horiuti, *Z. Physik*, 1933, **84**, 380.

[17] A. Adel and E. F. Barker, *J. Chem. Physics*, 1934, **2**, 627.

[18] D. M. Dennison, *Rev. Mod. Physics*, 1931, **3**, 280; L. Tisza, *Z. Physik*, 1933, **82**, 48.

Although these selection rules will usually enable a definite model to be chosen for the molecule (*viz.*, one having the required degree of symmetry) the final assignment of particular fundamental frequencies to particular modes of vibration can only be made completely certain by an examination of the rotational fine structure of some of the observed bands. So far, this is only practicable in absorption, since Raman scattering in the gas is too weak (with present methods) to give more than the central (Q) maximum of the band. Even in absorption, we are seriously limited by the low resolving power of the spectrometer. Up to the present, the smallest line separation which can be resolved is of the order of 0·5 cm.$^{-1}$. To realise the full import of this limitation, it is necessary to consider the rotational fine structure of the different classes of molecule in a little detail.

Linear molecules. There are two types of band, and two only, according as the vibration of the electric moment takes place along, or perpendicular to, the symmetry axis of the molecule. The line spacing in each is the same and is given by $h/4\pi I_A$ in frequency units. The linear molecules for which it has been possible to resolve this spacing are carbon dioxide, nitrous oxide, hydrogen cyanide, and acetylene.[10a] It seems unlikely that many more complicated molecules can be investigated in this way since the spacing for nitrous oxide [19] is already only 0·8 cm.$^{-1}$. In cases of heavier molecules, however, it is possible to make an estimate of the moment of inertia by measuring the spacing between the intensity maximum of the P and the R branch of the band, which is given by the classical formula of Bjerrum, $(\sqrt{kT/I_A})/\pi$.[20] This has been done for carbon disulphide.[21]

Symmetrical top molecules. There are again two types of band. The first corresponds to vibration of the electric moment along the symmetry axis of the molecule, and resembles very closely the perpendicular type band of a linear molecule. The spacing of the lines is given by $h/4\pi^2 I_A$, and so gives no information about the moment of inertia I_C. The other type of band associated with vibration of the electric moment perpendicular to the symmetry axis of the molecule is very complicated indeed, consisting of sets of overlapping bands. The spacing between the lines depends on both of the moments of inertia, and so, knowing I_A from the parallel bands, one might expect the deduction of I_C from the perpendicular bands to be an easy matter. That this is far from being the case is due to two causes: first, the excessive number of lines makes them incapable of resolution except in a few favourable cases (*viz.*, where $I_A \gg I_C$), and secondly, the spacing (when it can be determined) is not found to be the same in the different bands. The latter phenomenon has long worried spectroscopists, and it is only in the past year that this difficulty has been completely resolved. The qualitative explanation was first given by E. Teller and L. Tisza,[22] who showed that it was due to the imperfect coupling which may exist between rotation of the molecule and degenerate vibrations of this type in a symmetrical molecule. To put it very roughly, the vibration itself may have a characteristic angular momentum which can be coupled to that due to rotation of the molecule as a whole. It is readily understandable that such a phenomenon would lead to anomalous spacings, as the coupling factor need not be the same for each mode of vibration. More recently, E. Teller [23] gave a quantitative theory, in which he showed that although the spacings in the separate bands could not be predicted without a knowledge of the force constants controlling the vibrations, yet the sum of the spacings in all the bands was a function only of the masses and of the inter-nuclear distances in the molecule. Unfortunately, Teller's work contained some errors, but M. Johnson and D. M. Dennison [24] have finally given the simplest expression for the sum of the spacings in terms of the moments of inertia of the molecule. Thus, they were able for the first time to give accurately the moments of inertia of methane and the methyl halides. In cases where the moments of inertia are so large that it is impossible to resolve the individual rotation lines, a fair estimate of them may be obtained by a careful measurement of the separation and intensity of the two extreme maxima in the " parallel " bands.[25]

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[19] E. K. Plyler and E. F. Barker, *Physical Rev.*, 1931, **38**, 1827.

[20] Here k is Boltzmann's constant, and T the absolute temperature.

[21] C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc.*, 1931, [*A*], **132**, 236; *ibid.*, 1933, [*A*], **140**, 605.

[22] *Z. Physik*, 1932, **73**, 791.

Asymmetrical top molecules. For these molecules the position is not nearly so simple. Here, as we have said, there is no explicit expression for the rotational energy, but to each value of the rotational quantum number J there correspond $2J + 1$ levels, and the selection rules governing transitions between all these levels cannot be given in a short space. The resulting band structure is extremely complex and apparently hopelessly irregular. However, given patience and a rough idea of the values of the moments of inertia, there is no reason why it should not be analysed and this has been accomplished successfully for water,[26] hydrogen sulphide,[27] formaldehyde,[28] and ethylene.[29] It will be noticed that each of these molecules contains at least one hydrogen atom, and it is very unlikely that any asymmetrical top molecule not containing a hydrogen atom will have its vibration–rotation analysed for a long time to come. The resolving power of present spectrometers will have to be improved by an order of magnitude before sufficient structure will be obtained to justify an attempt at analysis. Yet the position is not so hopeless as this sounds, for, as in the other types of molecule, the contour of the unresolved band gives some guide as to its form.[30] Thus, it appears that the contour of a band which corresponds to a vibration of the electric moment along the greatest axis of inertia will exhibit a strong but rather broad central (Q) maximum together with symmetrically disposed minor (P and R) maxima. For a vibration along the middle axis of inertia, one would expect the central (Q) branch to be absent, while for a vibration along the least axis of inertia, a very sharp and well-defined Q branch is to be expected in addition to the " P " and " R " maxima. These qualitative rules are well exemplified in the spectra of water,[31] hydrogen sulphide,[32] ethylene,[33] and sulphur dioxide,[34] but attempts to apply them quite generally, *e.g.*, to ozone [35] and nitrogen peroxide,[36] have led to difficulties. This is not surprising seeing that they are only an extrapolation from calculations on the possible transitions for $J < 5$. It may be that future theoretical work will lead to their being modified for heavier molecules.

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[23] *Loc. cit.*, ref. (7).

[24] *Physical Rev.*, 1935, **47**, 93; **48**, 868.

[25] S. L. Gerhard and D. M. Dennison, *ibid.*, 1933, **43**, 197.

[26] R. Mecke, *Z. Physik*, 1933, **81**, 313; R. Mecke and W. Baumann, *ibid.*, p. 445; K. Freundenberg and R. Mecke, *ibid.*, p. 465.

[27] P. C. Cross, *Physical Rev.*, 1935, **47**, 7.

[28] H. H. Nielsen, *ibid.*, 1934, **46**, 117.

[29] R. M. Badger, *ibid.*, 1934, **45**, 648.

[30] D. M. Dennison, *Rev. Mod. Physics*, 1931, **3**, 280.

To sum up, it is now possible to determine the general form and fundamental frequencies of the simpler polyatomic molecules, and to assign each fundamental to a particular mode of vibration of the model. Only in the hydrogen-containing molecules (and a few linear ones such as carbon dioxide or carbonyl sulphide) does it seem possible to obtain accurate values of the moments of inertia without a great increase in resolving power of spectrometers in the infra-red. The only obvious line of advance would be to observe overtones (instead of fundamentals), which fall in the photographic region. Unfortunately, it is just those molecules whose overtones have a measurable intensity in the photographic region, *viz.*, the hydrogen-containing ones, which are already analysed.

C. *Electronic spectra.* Although an immense amount of work has been done on the electronic spectra of polyatomic molecules, there is remarkably little which can be said to be of significance from the true spectroscopic point of view; in other words, very little of it can be interpreted to yield the energy states of the absorbing or emitting molecule. This is not surprising, since the theory of such spectra has only been developed in the last three years. The first step was made by R. S. Mulliken [37] who showed how the electronic levels may be classified by means of their symmetry properties, and by extrapolating from close analogies with well-known diatomic spectra. G. Herzberg and E. Teller, and others,[38] have now considered the selection rules which govern the associated vibrational transitions, while the rules for the rotational transitions follow readily from those applicable to vibration–rotation spectra. To go into all these matters in detail is impossible in the space allotted, and we reserve their discussion for a future Report. We can now only mention a few of the more successful attempts to apply and test the theory.

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[31] E. K. Plyler and W. W. Sleator, *Physical Rev.*, 1931, **37**, 1493; and ref. (26).

[32] A. D. Sprague and H. H. Nielsen, *ibid.*, 1933, **43**, 375.

[33] A. Levin and C. F. Meyer, *J. Opt. Soc. Amer.*, 1928, **16**, 137.

[34] C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc.*, 1932, [*A*], **137**, 622; C. R. Bailey, A. B. D. Cassie, and W. R. Angus, *ibid.*, 1930, **130**, 133.

[35] G. Hettner, R. Pohlmann, and H. J. Schumacher, *Z. Physik*, 1934, **91**, 372.

[36] G. B. B. M. Sutherland and W. G. Penney, *Nature*, 1935, **135**, 958.

[37] *Physical Rev.*, 1932, **40**, 55; **41**, 49; 1933, **43**, 279; *J. Chem. Physics*, **1933**, **1**, 492; 1935, **3**, 375, 506, 514, 517, 564, 635, 720.

The first electronic spectrum to be analysed was that of formaldehyde. The rotational structure of several bands was analysed by G. H. Dieke and G. B. Kistiakowsky,[39] enabling them to give the moments of inertia of the molecule in the ground and excited states with considerable accuracy. The interpretation of the electronic transition and the deduction of the nature of the electronic states is due to R. S. Mulliken.[40] Another important success was achieved in the methyl halides,[41] although in this case the rotational structure cannot yet be satisfactorily resolved. E. Eastwood and C. P. Snow[42] have examined the spectra of a series of aldehydes; it appears from their results that these are not due (as was formerly supposed) to the excitation of an electron in the carbonyl bond, but to the excitation of one of the non-localised electrons of the carbon atom. They also obtained some remarkably simple bands from acraldehyde, which could best be represented as isolated *R* branches fitting the usual parabolic formula. Unfortunately, these do not give consistent values for the corresponding "moment of inertia" and their explanation is at present obscure. Other molecules with which some progress has been made are SO_2,[43] C_2H_2,[44] C_2H_4,[45] NH_3,[46] CO_2,[47] CS_2,[48] HCN,[49] and N_2H_4.[49]

There is one very important advance on the experimental side to be reported. This is the development of a new type of Lyman continuum for the extreme ultra-violet by G. Collins and W. C.

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[38] *Z. physikal. Chem.*, 1933, [*B*], **21**, 410. Also A. B. F. Duncan, *J. Chem. Physics*, 1935, **3**, 384.

[39] *Physical Rev.*, 1934, **45**, 4.

[40] *Ibid.*, 1935, **47**, 413.

[41] Refs. (38) and (40).

[42] *Proc. Roy. Soc.*, 1935, [*A*], **149**, 434.

[43] J. H. Clements, *Physical Rev.*, 1935, **47**, 224; R. K. Asundi and R. Samuel, *Proc. Indian Acad. Sci.*, 1935, **2***A*, 30.

[44] W. C. Price, *Physical Rev.*, 1934, **45**, 843; *ibid.*, 1935, **47**, 444; H. Göpfert, *Z. wiss. Phot.*, 1935, **34**, 156.

[45] H. J. Hilgendorff, *Z. Physik*, 1935, **95**, 781; see also refs. (38) and (44).

[46] A. B. F. Duncan, *Physical Rev.*, 1935, **47**, 822.

[47] *Idem*, *J. Chem. Physics*, 1935, **3**, 384.

[48] W. W. Watson and A. E. Parker, *Physical Rev.*, 1931, **37**, 1013; and ref. (47).

[49] H. J. Hilgendorff, *Z. Physik*, 1935, **95**, 781.

Price.[50] As a result, W. C. Price [51] has been able to photograph absorption spectra of many polyatomic molecules as far down as 300 Å. He has found the very interesting result that most of the simple molecules exhibit bands in this region which can be arranged in Rydberg series. He has thus been able to find the ionisation potentials of several of the simpler molecules such as acetylene, ethylene, water, hydrogen sulphide, and the methyl and ethyl halides.

Spectra of Deuterium Compounds.—The early work on the spectra of deuterium and its simpler compounds has already been reviewed ;[52] this report is accordingly confined almost entirely to work which has appeared during the past year. For the best documented and detailed report of the early work the review of H. C. Urey and G. K. Teal [53] is, of course, the standard reference. Work on the spectra of deuterium compounds has, roughly speaking, one of four objects in view : (1) the investigation of the accurate theory of the isotope effect in diatomic spectra and the elucidation of certain perturbation problems in such spectra, (2) the determination and assignment of doubtful fundamental frequencies in polyatomic molecules, (3) the determination of internuclear distances in polyatomic molecules containing hydrogen, and (4) the determination of potential functions for polyatomic molecules.

As regards (1), certain difficulties arose when it was found by W. Holst and E. Hulthén [54] that the " *B* values " (these define the spacing of the rotational structure of the band) did not have the expected ratio for AlH and AlD. These authors explained this as due to the neglect of the moment of inertia of the electron cloud. R. de L. Kronig,[55] however, gave an entirely different explanation based on the fact that a certain interaction term giving the reaction of the nuclei to the precession of the electronic angular momentum had been neglected. Unfortunately, Kronig's theory cannot give the whole truth for, according to it, there should be no anomaly for DCl, LiD, or NaD. Now, although the first does not have the anomaly,[56] the other two do.[57] The whole theory has been carefully reviewed by G. H. Dieke,[58] who has shown that Kronig's theory

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[50] *Rev. Sci. Instr.*, 1934, **5**, 423.

[51] Ref. (44); *J. Chem. Physics*, 1935, **3**, 256.

[52] *Ann. Reports*, 1933 and 1934.

[53] *Rev. Mod. Physics*, 1935, **7**, 34.

[54] *Z. Physik*, 1934, **90**, 712.

[55] *Physica*, 1934, **1**, 621.

[56] J. D. Hardy, E. F. Barker, and D. M. Dennison, *Physical Rev.*, 1932, **42**, 279.

[57] F. H. Crawford and T. Jorgensen, *ibid.*, 1934, **46**, 746; E. Olsson, *Z. Physik*, 1935, **93**, 206, 816.

[58] *Physical Rev.*, 1935, **47**, 661; **48**, 606; G. H. Dieke and R. W. Blue, *ibid.*, 1935, **47**, 261.

(supplemented by corrections for anharmonic factors) will account completely for the isotope effect in the spectra of HD and D_2, but that it is not capable of explaining the defects of heavier molecules. Since then, more experimental work has been done,[59] and the importance of anharmonic corrections demonstrated.[60] The complete theoretical explanation is still, however, some way from achievement.

The determination and assignment of doubtful fundamental frequencies by means of the isotope effect is likely to become one of the more important applications of the discovery of deuterium to spectroscopy. A very striking example is afforded by benzene, for which there has long been the anomaly that certain of the Raman frequencies appear to coincide with fundamental absorption frequencies in the infra-red. The apparent conclusion that the benzene molecule does not have a centre of symmetry has not found favour in view of the theory of "resonance" between possible Kekulé structures. If, however, this coincidence of infra-red and Raman frequencies were purely fortuitous, then it would not be expected to occur for the isotopic form, hexadeuterobenzene. Recent work here [61] and in America,[62] although not yet final, all tends to show that the agreement was indeed fortuitous, and that benzene is symmetrical. Other applications towards the assignment and identification of fundamentals have been made in the cases of water,[63] ammonia, phosphine,[64] and chloroform.[65]

In the third type of application we would mention the accurate determination of all the internuclear distances in the molecules acetylene,[66] hydrogen cyanide,[67] methane,[68] and ammonia.[68a] The final and possibly most important application is in connexion with the determination of the most suitable potential function to represent the force field controlling the vibration of the atoms in a polyatomic molecule. Many attempts have been made to do this,[69] but none has been more than partially successful, since more constants are required to define the force field than there are frequencies by which to determine them. The introduction of a deuterium in place of a hydrogen atom leaves the force field unchanged (to the degree of approximation involved here) while yielding a new set of frequencies. The problem then is no longer indeterminate. Conversely, any force field which was chosen in an empirical way to agree with the earlier data, may now be tested by seeing how well it predicts the frequencies of the deuterium compound. The general theory of the isotope effect has been given by several authors;[70] applications have already been made to acetylene,[71] water,[72] hydrogen cyanide,[67] ammonia,[73] phosphine,[64] methane, and the methyl halides.[74] G. B. B. M. S.

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[59] F. H. Crawford and T. Jorgenson, *Physical Rev.*, 1935, **47**, 358, 932; W. W. Watson, *ibid.*, p. 27; A. Guntsch, *Z. Physik*, 1935, **93**, 534; B. Grundstrom, *ibid.*, 1935, **95**, 574; Y. Fujioka and T. Wada, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **27**, 210.

[60] P. G. Koontz, *Physical Rev.*, 1935, **48**, 138.

[61] W. R. Angus, C. R. Bailey, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, *Nature*, 1935, **135**, 1033; **136**, 680.

[62] R. B. Barnes and R. R. Brattain, *J. Chem. Physics*, 1935, **3**, 446; R. W. Wood, *ibid.*, **3**, 444.

[63] C. H. Cartwright, *Nature*, 1935, **136**, 181; R. Ananthakrishnan, *Mem. Ind. Inst. Sci.*, 1935, **2**, No. 21, 291.

[64] J. B. Howard, *J. Chem. Physics*, 1935, **3**, 207.

[65] R. W. Wood and D. H. Rank, *Physical Rev.*, 1935, **48**, 63.

[66] G. Herzberg, F. Patat, and J. W. T. Spinks, *Z. Physik*, 1934, **92**, 87.

[67] P. F. Bartunek and E. F. Barker, *Physical Rev.*, 1935, **48**, 516.

[68] N. Ginsburg and E. F. Barker, *ibid.*, 1935, **47**, 641; *J. Chem. Physics*, 1935, **3**, 668.

[68a] R. B. Barnes, *Physical Rev.*, 1935, **47**, 658; E. F. Barker and M. Migeotte, *ibid.*, p. 702.

4. THE DETERMINATION OF THERMODYNAMIC CONSTANTS FROM SPECTROSCOPIC DATA BY STATISTICAL METHODS.

The energy of a molecule may be divided into two independent parts: one is concerned with translation only, and the other involves all forms of internal energy. The portion, due to translation, of a thermodynamic function, *e.g.*, entropy, total energy, or heat capacity, of *any* molecule in the ideal gaseous state is virtually the whole of the value for a monatomic gas. This problem has been treated by a number of authors,[1] and the equation for the entropy of a monatomic gas—the well-known Sackur–Tetrode equation—may be written

$$S = R[\ln(2\pi kmT)^{3/2}V/h^3N + \tfrac{5}{2}] \quad . \quad . \quad . \quad (1)$$

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[69] See *Ann. Reports*, 1934, **31**, 21; J. E. Rosenthal, *Physical Rev.*, 1934, **45**, 426; **46**, 730; *ibid.*, 1935, **47**, 235; G. B. B. M. Sutherland and D. M. Dennison, *Proc. Roy. Soc.*, 1935, [*A*], **148**, 250; A. B. D. Cassie, *ibid.*, p. 87.

[70] E. Teller, *loc. cit.*, ref. (7); O. Redlich, *Z. physikal. Chem.*, 1935, [*B*], **28**, 371; J. E. Rosenthal, *loc. cit.*

[71] G. B. B. M. Sutherland, *Nature*, 1934, **134**, 775; W. F. Colby, *Physical Rev.*, 1935, **47**, 388; Y. Morino, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **25**, 232; **27**, 39; see also ref. (66).

[72] L. G. Bonner, *Physical Rev.*, 1934, **46**, 458; J. E. Rosenthal, *loc. cit.*, ref. (69); R. Ananthakrishnan, *loc. cit.*, ref. (63).

[73] M. F. Manning, *J. Chem. Physics*, 1935, **3**, 136; see also ref. (64).

[74] M. Johnson and D. M. Dennison, *Physical Rev.*, 1935, **47**, 93; **48**, 868.

[1] O. Sackur, *Ann. Physik*, 1911, **36**, 958; 1913, **40**, 67; *A.*, 1912, ii, 145; 1913, ii, 128; H. Tetrode, *ibid.*, 1912, **38**, 434; 1913, **39**, 255; O. Stern, *Physikal. Z.*, 1913, **14**, 629; *Z. Elektrochem.*, 1919, **25**, 66; *A.*, 1919, ii, 219; P. Ehrenfest and V. Trkal, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 162; *Ann. Physik*, 1921, **65**, 609; *A.*, 1920, ii, 738; L. S. Kassel, *Chem. Reviews*, 1936, in the press.

where R is the gas-constant, k the Boltzmann constant, m the weight of a single molecule, T the absolute temperature, V the volume of 1 g.-mol. in c.c., h the Planck constant, and N the Avogadro number. This expression represents the translational entropy of any ideal gas, and for practical purposes at 1 atm. pressure, it may be put in the form

$$S^\circ_{\text{tr.}} = \tfrac{3}{2}R \ln M + \tfrac{5}{2}R \ln T - 2{\cdot}300 \quad . \quad . \quad . \quad (2)$$

R is now expressed in calories, and M is the molecular weight of the gas. Similarly the translational energy of any gas has the value $\frac{3}{2}RT$ per g.-mol., and the corresponding heat capacity is $\frac{3}{2}R$; these results follow, of course, from the kinetic theory.

For polyatomic molecules the portion of the various thermodynamic functions due to internal energy must now be considered.[2] If the Maxwell–Boltzmann distribution law applies to a system, then the number of molecules in any state represented by i, is $p_iAe^{-\varepsilon_i/kT}$, p_i being the " *a priori* probability " or " statistical weight " of the ith state, A the number of molecules in the state of lowest internal energy, and ε_i the internal energy per molecule in the given state, with reference to the lowest energy state.* The statistical weight represents the degeneracy, or multiplicity, of the energy level under consideration : in terms of wave mechanics it is the number of proper values (eigenvalues) which satisfy the wave equation for the molecule in the particular quantum state. Actually these values do not correspond to states of identical energy, but the differences are so small that they may be grouped together in one state with a probability p equal to the number of eigenvalues. In 1 g.-mol. of a gas the total number of molecules, *i.e.*, the Avogadro number, is equal to the sum of the molecules in the various states characterised by $i = 0, 1, 2, 3, \ldots$; hence $N = A\Sigma pe^{-\varepsilon/kT}$. Similarly, the internal energy of all the molecules in a given state is $\varepsilon pAe^{-\varepsilon/kT}$, and the total internal energy $E^\circ_{\text{int.}}$ of 1 g.-mol. of gas, *with reference to the zero state*, is $A\Sigma\varepsilon pe^{-\varepsilon/kT}$. Combining this relationship with the equation for N, it follows that

$$E^\circ_{\text{int.}} = N\Sigma\varepsilon pe^{-\varepsilon/kT}/\Sigma pe^{-\varepsilon/kT} = RT^2\, d\ln Q/dT \quad . \quad (3)$$

[2] The treatment given here is essentially that of W. F. Giauque, *J. Amer. Chem. Soc.*, 1930, **52**, 4808.

* The convention adopted in the treatment given here is to take as the zero the energy of the molecule at rest and with vibrational and rotational quantum numbers equal to zero ; *i.e.*, the value of ϵ is effectively the difference between the total energy and the zero-point energy (the energy at 0° Abs.). It will be seen later (p. 70) that some authors take the molecule in its dissociated state, *i.e.*, in the form of atoms, to represent the zero from which to take the ϵ values. Whichever convention is adopted, the final result must be the same (compare R. H. Fowler, " Statistical Mechanics," 1929, p .26, footnote).

where Q is equal to $\Sigma pe^{-\varepsilon/kT}$, and is known as the "summation of state" or "state sum" ("Zustandsumme," Planck) or "partition function" (Fowler). Strictly speaking, the equation given applies only if the Maxwell–Boltzmann distribution holds, and this is certainly not the case for real gases, especially at low temperatures; the assumption of an ideal gas, however, permits the use of the classical law, and in any case at appreciable temperatures the Bose–Einstein and Fermi–Dirac statistics lead to the same result.[3]

The differentiation of $E^\circ_{\text{int.}}$ with respect to temperature gives an expression for the heat capacity of a perfect gas due to internal degrees of freedom,[4] thus

$$\frac{dE^\circ_{\text{int.}}}{dT} = C_{\text{int.}} = \left(\frac{R}{T^2}\right)\frac{d^2 \ln Q}{d(1/T)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$= \frac{N^2}{RT^2}\left[\frac{\Sigma\varepsilon^2 pe^{-\varepsilon/kT}}{\Sigma pe^{-\varepsilon/kT}} - \left(\frac{\Sigma\varepsilon pe^{-\varepsilon/kT}}{\Sigma pe^{-\varepsilon/kT}}\right)^2\right] . \qquad (5)$$

Alternatively, this equation can be written [5]

$$C_{\text{int.}} = \frac{N^2}{RT^2}\left[\frac{\Sigma C}{\Sigma A} - \left(\frac{\Sigma B}{\Sigma A}\right)^2\right] \quad . \quad . \quad . \quad . \qquad (6)$$

where $\Sigma A = Q$; $\Sigma B = kT^2(dQ/dT)$; and $\Sigma C = 2k^2T^3(dQ/dT) + k^2T^4(d^2Q/dT^2)$.

By making use of the definition of internal entropy in the form $dS_{\text{int.}} = C_{\text{int.}}\, d\ln T$, it follows that the entropy [6] due to internal degrees of freedom is given by

$$S^\circ_{\text{int.}} = R[\ln Q + T\, d\ln Q/dT] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

$$= R[\ln A + (1/kT)(\Sigma B/\Sigma A)] \quad . \quad . \quad . \quad . \qquad (8)$$

$$= R[\ln \Sigma pe^{-\varepsilon/kT} + \Sigma\varepsilon pe^{-\varepsilon/kT}/kT\Sigma pe^{-\varepsilon/kT}] \quad . \qquad (9)$$

From any of these equations it is possible to calculate the internal entropy of an ideal gas, and the addition of the translational entropy, equation (2), gives the value of S°, the total entropy at atmospheric pressure. If necessary, a correction can be applied for deviations from ideal behaviour, but this is quite small, especially at temperatures high enough to be of chemical interest.[7]

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[3] W. F. Giauque, *loc. cit.*; G. N. Lewis and J. E. Mayer, *Proc. Nat. Acad. Sci.*, 1929, **15**, 208; *A.*, 1929, 648; W. H. Rodebush, *Chem. Reviews*, 1931, **9**, 319; H. L. Johnston and M. K. Walker, *J. Amer. Chem. Soc.*, 1933, **55**, 182 (footnote).

[4] Cf. F. Reiche, *Ann. Physik*, 1919, **58**, 657; H. C. Urey, *J. Amer. Chem. Soc.*, 1923, **45**, 1445; *A.*, 1923, ii, 533; R. C. Tolman and R. M. Badger, *ibid.*, 1923, **45**, 2277; *A.*, 1923, ii, 830; H. C. Hicks and A. C. G. Mitchell, *ibid.*, 1926, **48**, 1520; *A.*, 1926, 784.

[5] H. L. Johnston and A. T. Chapman, *ibid.*, 1933, **55**, 153; *A.*, 1933, 229.

[6] H. C. Urey, *loc. cit.*; R. C. Tolman and R. M. Badger, *loc. cit.*; H. C. Hicks and A. C. G. Mitchell, *loc. cit.*

The free energy F° in the standard state, *i.e.*, ideal gas at 1 atm. pressure, may be expressed

$$F^\circ = E^\circ + RT - TS^\circ \quad . \quad . \quad . \quad . \quad (10)$$

where E° and S° refer to the *total* energy and entropy, respectively, including the translational terms. The total energy E° must also include the energy of the gas at assumed zero state, *i.e.*, the zero-point energy ($E_0{}^\circ$), in addition to the energy of translation ($\frac{3}{2}RT$), and the internal energy ($E^\circ{}_{\text{int.}}$) obtained from equation (3). It follows, therefore, that

$$F^\circ - E_0{}^\circ = -\tfrac{3}{2}RT\ln M - \tfrac{5}{2}RT\ln T - RT\ln Q + 7{\cdot}267T \quad (11)$$

By combining the $F^\circ - E_0{}^\circ$ values for resultants and reactants, it is possible, provided Q be known, to determine $\Delta(F^\circ - E_0{}^\circ)$ for a chemical reaction, and this is related to the thermodynamic equilibrium constant. By definition, in this case, $\Delta F^\circ = -RT\ln K_p$ with pressures in atms., and hence

$$-\Delta(F^\circ - E_0{}^\circ) = RT\ln K_p + \Delta E_0{}^\circ \quad . \quad . \quad (12)$$

The calculation of K_p for a reaction involves a knowledge of $-\Delta(F^\circ - E_0{}^\circ)$ for the substances concerned in the process, evaluated from equation (11), and of $\Delta E_0{}^\circ$ for the reaction as a whole. The latter quantity may be determined by combining appropriate spectroscopic data for heats of dissociation, since these are values for the lowest energy level, or by means of the zero-point energies of the molecules, including all modes of vibration, also obtained from band spectra. The $E_0{}^\circ$ for an atom must be stated on the basis of the assumed energy zero as a *molecule.* Alternatively, if ΔH°, the heat of reaction at constant pressure, is known, then since $H^\circ = E^\circ + RT$, it can be readily shown, by means of equation (10), that

$$\Delta E_0{}^\circ = \Delta H^\circ - \Delta[\tfrac{5}{2}RT + RT^2(d\ln Q/dT)] \quad . \quad (13)$$

The factor $+ 7{\cdot}267$ in equation (11) arises, as may be seen from a consideration of this and equations (1) and (2), from the term $R\ln(2\pi k/h^2N)^{3/2}k/a$, where a is the normal atmosphere in dynes per sq. cm., *i.e.*, $1{\cdot}0132 \times 10^6$, and if this is introduced into equation (11) it becomes

$$F^\circ - E_0{}^\circ = -RT\ln[Q(2\pi mkT/h^2)^{3/2}kT/a] \quad . \quad (14)$$

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[7] See, *e.g.*, W. F. Giauque, *J. Amer. Chem. Soc.*, 1930, **52**, 4822; A. R. Gordon, *J. Chem. Physics*, 1933, **1**, 308.

A further obvious modification leads to

$$F^\circ = - RT \ln \{[e^{-E_0^\circ/RT} Q (2\pi mkT/h^2)^{3/2}](kT/a)\} \quad . \quad (15)$$

$$= - RT \ln G(kT/a)\,^{*} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where G is equal to the term in the square brackets. For any reversible chemical reaction $a\mathrm{A} + b\mathrm{B} \ldots \rightleftharpoons m\mathrm{M} + n\mathrm{N} \ldots$, it is evident, since $\Delta F^\circ = - RT \ln K_p$ that

$$K_p = \frac{G_\mathrm{M}{}^m \times G_\mathrm{N}{}^n \times \ldots}{G_\mathrm{A}{}^a \times G_\mathrm{B}{}^b \times \ldots} \times (kT/a)^\nu \quad . \quad . \quad . \quad (17)$$

where $\nu = (m + n + \ldots) - (a + b + \ldots)$. Some authors omit the factor $(kT/a)^\nu$, thus giving K_c with concentrations expressed in molecules per c.c., whereas others omit a only, which gives K_p with pressures in dynes per sq. cm. instead of in atmospheres. If ν is zero the K's are, of course, all identical. The quantity G, which may be regarded as the *complete* partition function of any molecular species under given conditions, is made up of three separate terms. The portion $(2\pi mkT/h^2)^{3/2}$ is effectively the partition function for translatory motion with three degrees of freedom,[8] and Q is the function for vibration and rotation, including nuclear-spin effects and internal rotation within the molecule; there still remains the " zero-point " factor $e^{-E_0^\circ/RT}$. If the zero of energy, for the purpose of calculating the vibrational and rotational partition function, is taken as the energy of the free atoms,[9] formed by the molecule when completely dissociated, at their lowest levels, then a quantity $e^{-E_0'/RT}$ actually becomes included in the vibrational function, E_0' being the heat of dissociation of the molecule at 0° Abs. The energy term in the " zero-point " factor is altered by this same amount, thus leading to a value identical with G for the partition function.†

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[8] R. H. Fowler, " Statistical Mechanics," 1929, p. 114.

[9] *Idem, ibid.*, p. 103.

* The corresponding equation for hydrogen given by E. Teller and B. Topley (*J.*, 1935, 877) should not contain the E_0° term (private communication from Mr. B. Topley). The position of the large bracket also appears to have been misprinted.

† The subjects of equilibrium constants and partition functions have been dealt with at length because of the apparent confusion facing a newcomer to the literature. Writers who employ Q generally use it in the sense defined above, and Q' is often used for $e^{-E_0^\circ/RT} \times Q$, but not consistently. H. C. Urey and D. Rittenberg (*J. Chem. Physics*, 1933, **1**, 137) define Q without the zero-point factor, but H. C. Urey and G. K. Teal (*Rev. Mod. Physics*, 1935, **7**, 52) include it in some cases, although not in others. H. C. Urey and L. J. Greiff (*J. Amer. Chem. Soc.*, 1935, **57**, 321) define the " summation of state," given the symbol Q, to include the $e^{-E_0^\circ/RT}$ term, and use f, which is equal to GkT, as the " distribution function." The " distribution function " f of R. H. Crist and G. A. Dalin (*J. Chem. Physics*, 1934, **2**, 735) is virtually

In order to apply the equations given above to evaluate thermodynamic constants, the essential point remaining is the determination of Q : to calculate this quantity the $pe^{-\varepsilon/kT}$ terms must be summed over *all possible* energy states of the molecule. The energy of each state can be obtained from spectroscopic data with the aid of the fundamental equation of the quantum theory, $\varepsilon = hc\nu$, but there is some difficulty in the assignment of the correct statistical weights (p); it was the use of incorrect values which invalidated the earlier applications [10] of some of the equations deduced here. The principles involved in the determination of the partition function, which are based on wave mechanics, may be conveniently considered separately for (*a*) atoms and monatomic molecules, (*b*) diatomic, and (*c*) more complex molecules.

Atoms and Monatomic Molecules.—The value of Q is given by the product of the function for nuclear-spin orientation and that for every possible electronic configuration. The nuclear-spin function is equal to the corresponding statistical weight, since ε is zero, and is given by $2i_s + 1$, where i_s is the number of units of nuclear-spin momentum; this quantity represents the total number of possible orientations, having nearly the same energy, of the nucleus in a perturbing field. The p factor for each electronic configuration is $2j_s + 1$, where $j_s(= l \pm s)$, which cannot be negative, results from the combination of the azimuthal quantum number (l) and the resultant spin (s) of the electrons; to obtain the partition function this weight must be multiplied by $e^{-\varepsilon/kT}$ for the appropriate state, and summed over all possible configurations indicated by spectroscopic data. This apparently impossible task is simplified by the fact that the quantity $e^{-\varepsilon/kT}$ has a significant value only at temperatures exceeding $hc\nu/4k$, where ν in cm.$^{-1}$ is the frequency separation of the given energy level above the ground level.[11] Hence, it is only at high temperatures that any level other than the ground state ($\varepsilon = 0$) need be considered. With atomic hydrogen, for

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identical with our G, and so also, apparently, is the G of E. Teller and B. Topley (*J.*, 1935, 876), although the latter authors employ a different energy-zero convention. The partition function F employed by B. Topley and H. Eyring (*J. Chem. Physics*, 1934, **2**, 217) is evidently $e^{-E_0'/RT}$ times the product of Q and the translational factor; since $\Delta E_0'$ is equal to $\Delta E_0°$, this function F may replace G in the calculation of equilibrium constants. The partition function F used in chemical kinetics (see p. 94) is G with the zero-point factor omitted.

[10] H. C. Urey; R. C. Tolman and R. M. Badger; H. C. Hicks and A. C. G. Mitchell, *locc. cit.*, ref. (4); see also D. S. Villars, *Proc. Nat. Acad. Sci.*, 1929, **15**, 705; 1930, **16**, 396; *A.*, 1929, 1236; 1930, 1121.

[11] J. E. Mayer, S. Brunauer, and M. G. Mayer, *J. Amer. Chem. Soc.*, 1933, **55**, 37; *A.*, 1933, 218; H. Zeise, *Z. Elektrochem.*, 1933, **39**, 762.

example,[12] $i_s = \frac{1}{2}$, and so the corresponding partition function is 2; the electronic ground level ($n = 1$) is a singlet state with $j_s = \frac{1}{2}$, and since $\varepsilon = 0$, the electronic function is also 2. Since no higher level need be considered, the complete partition function is 4, there being no vibrational or rotational energy for an atom. The nuclear spin of the chlorine atom is $\frac{5}{2}$, and so the nuclear-spin function is 6; spectroscopic evidence indicates the ground state to be an inverted ^2P doublet, with j_s values of $\frac{3}{2}$ for the lower and $\frac{1}{2}$ for the upper level, the frequency separation being 881 cm.$^{-1}$. The statistical weights for the two levels, *i.e.*, $2j_s + 1$, are 4 and 2, respectively, and hence the electronic partition function is $4 + 2e^{-881hc/kT}$; the complete function for the atom is then obtained by multiplying by 6 for the nuclear spin. No other energy levels need be considered for all reasonable temperatures.[13] The ground level of normal atomic oxygen is an inverted ^3P term, the j_s values being 2, 1, and 0, respectively, and the frequency separations 157·4 cm.$^{-1}$ and 226·1 cm.$^{-1}$; the electronic partition function is thus $5 + 3e^{-157 \cdot 4hc/kT} + 1e^{-226 \cdot 1hc/kT}$. At high temperatures it is also necessary to include the contributions for the two metastable levels consisting of $^1D_2$ and $^1S_0$ terms, respectively. Since the oxygen nucleus has no spin, $i_s = 0$, the complete partition function is the same as the electronic contribution.[14] The literature may be consulted for other cases, which present no novel features.[15]

Diatomic Molecules.—The Q value for a molecule containing two or more atoms involves summation over every possible electronic, vibrational, and rotational state; in general, electronic levels above the ground state need not be considered, for reasons already given. The multiplicity, if any, of the ground level must, however, be included. Most diatomic molecules have $^1\Sigma$ ground terms, and so there are no multiplet levels; nitric oxide, oxygen, hydroxyl, and the cyanide radical, amongst others, are, however, exceptional.[16]

The energy separation of successive vibrational levels is relatively small, and so it is necessary to sum the $pe^{-\varepsilon/kT}$ terms over several levels; unless approximation methods are used (see below), only a few of the lowest states are actually included, especially at low temperatures. For example, with hydrogen it is only the lowest vibrational level ($v = 0$) which contributes appreciably to the partition function at temperatures below 900° Abs.; even at 2000° Abs. only the first four levels ($v = 0, 1, 2, 3$) need be considered.[17] With oxygen and nitric oxide, however, five levels must be included below 900° Abs., the number increasing up to 12 at 2000° Abs., in each multiplet.[18]

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[12] W. F. Giauque, *J. Amer. Chem. Soc.*, 1930, **52**, 4816; *A.*, 1931, 294.

[13] W. F. Giauque and R. Overstreet, *ibid.*, 1932, **54**, 1731; *A.*, 1932, 695.

[14] H. L. Johnston and M. K. Walker, *ibid.*, 1933, **55**, 187; *A.*, 1933, 229; G. van Elbe and B. Lewis, *ibid.*, p. 507; *A.*, 1933, 350.

[15] W. F. Giauque and J. O. Clayton, *ibid.*, p. 4875; *A.*, 1934, 135; H. L. Johnston and E. A. Long, *J. Chem. Physics*, 1934, **2**, 389; *A.*, 1934, 951; C. W. Montgomery and L. S. Kassel, *ibid.*, 1934, **2**, 417; *A.*, 1934, 966; H. Zeise, *Z. Elektrochem.*, 1934, **40**, 665.

[16] W. Jevons, "Band Spectra of Diatomic Molecules," 1932, Appendix II.

Each rotational state has, in addition to the rotational degeneracy resulting from nuclear spin, a statistical weight of $2J + 1$, where J is the rotational quantum number. If the molecule has two similar nuclei with spin i_s, the total statistical weight of each rotational level in a Σ^+ state is obtained by multiplying the $2J + 1$ value by the nuclear-spin factor $(i_s + 1)(2i_s + 1)$, for even values of J (including zero), and by $i_s\,(2i_s + 1)$ for odd values of J, if the nuclei follow the Bose–Einstein statistics, but the factors are reversed if the Fermi–Dirac statistics are followed. Ordinary hydrogen obeys the latter statistics, and since $i_s = \frac{1}{2}$, even levels have p values equal to $2J + 1$, and for odd levels they are $3(2J + 1)$, resulting in the well-known alternation of the spectral lines, and the proportions of *o*- and *p*-hydrogen in the normal gas. Deuterium molecules, on the other hand, have $i_s = 1$, and follow the Bose–Einstein statistics;[19] hence the statistical weights for even and odd levels are $2(2J + 1)$ and $2J + 1$, respectively.

The nuclear spin of the oxygen atom is zero, and consequently for the symmetrical $O^{16}O^{16}$ molecule, the main constituent of oxygen gas, alternate rotational levels have statistical weights of $2J + 1$ and zero; only alternate rotational levels, for odd values of J, are consequently present, the normal state being ${}^3\Sigma_g^-$ and the Bose–Einstein statistics being followed.[20] The components of the triplet term have been called the F_1, F_2, and F_3 coupling states (Hund's case-b). The coupling energy of the F_2 state is about 2 cm.$^{-1}$ (*ca.* 6 cals.): this amount is so small that all three states may be regarded as having the energy of the lowest level, *i.e.*, $\varepsilon = 0$. The value of J in calculating the rotational statistical weight is determined by the rotational quantum numbers, which are $K + 1$, K, and $K - 1$, respectively, for the levels F_1, F_2, and F_3, only odd values of K being permitted; the corresponding p values are, therefore, $2K + 3$, $2K + 1$, and $2K - 1$, where K has the values 1, 3, 5, etc. The rotational contribution to the partition function is then given by the three summations [21]

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[17] C. O. Davis and H. L. Johnston, *J. Amer. Chem. Soc.*, 1934, **56**, 1045; *A.*, 1934, 722.

[18] H. L. Johnston *et al.*, *ibid.*, 1933, **55**, 153, 172; *A.*, 1933, 229.

[19] G. N. Lewis and M. F. Ashley, *Physical Rev.*, 1933, **43**, 837; H. C. Urey and D. Rittenberg, *J. Chem. Physics*, 1933, **1**, 137; *A.*, 1934, 30.

[20] W. Jevons, *op. cit.*, p. 290, etc.

$$\sum_{K=1,3,5\ldots}(2K+3)e^{-\varepsilon_{F_1(K)}/kT}+\sum_{K=1,3,5\ldots}(2K+1)e^{-\varepsilon_{F_2(K)}/kT}+\sum_{K=1,3,5\ldots}(2K-1)e^{-\varepsilon_{F_3(K)}/kT}.$$

In addition to the ground state, two excited states, *viz.*, ${}^1\Delta_g{}^+$ at 0·97 e.v., and ${}^1\Sigma_g{}^+$ at 1·62 e.v., above the ground level, must be considered; the former [21] has a noticeable effect only at 1000° Abs., and the latter [22] at 2500° Abs.

If a diatomic molecule has two dissimilar nuclei, having spins i_s and i'_s, the nuclear-spin factor, by which the $2J+1$ value for *every* level is to be multiplied, is $(2i_s+1)(2i'_s+1)$ to obtain the complete rotational statistical weight. For a ${}^1\Sigma$ molecule, the application involves no complications, but where other types of ground terms have to be considered the necessary factors must be included. Nitric oxide in its ground state is ${}^2\Pi_{\frac{1}{2},\frac{3}{2}}$ (Hund's case-a coupling), with a frequency separation of about 120 cm.$^{-1}$, which is too large to be ignored; for the lower level the smallest value of J, here also the effective rotational quantum number, is $\frac{1}{2}$, whereas for the upper level it is $\frac{3}{2}$, subsequent values increasing in steps of unity. Except in Σ states, each rotational level is split into two slightly separated sub-levels, the phenomenon being known as Λ-type doubling.[23] The frequency separation of the doublet is generally so small that the energies may be regarded as identical, so that the effect is merely to double the statistical weights. The complete rotational partition function for nitric oxide is thus: [24]

$$2\times 3\sum_{J=\frac{1}{2},\frac{3}{2},\frac{5}{2}\ldots}(2J+1)e^{-\varepsilon_J/kT}+2\times 3\sum_{J=\frac{1}{2},\frac{3}{2},\frac{5}{2}\ldots}(2J+1)e^{-\varepsilon'_J/kT}$$

where 2 and 3 are the Λ-type doubling and the nuclear-spin factor, and ε_J and ε'_J refer to the energies in the ${}^2\Pi_{\frac{1}{2}}$ and the ${}^2\Pi_{\frac{3}{2}}$ state, respectively, for various values of J. At 298·1° Abs., no more than three values of J need to be included in each sum.

The hydroxyl radical has an inverted ${}^2\Pi$ ground term, so that the ${}^2\Pi_{\frac{3}{2}}$ is lower than the ${}^2\Pi_{\frac{1}{2}}$ level; the separation of rotational states into A and B sub-levels, due to Λ-type doubling, is unusually large, and so, except at high temperatures, it is not sufficient merely to double the statistical weights as is the case with nitric oxide. The rotational partition function is therefore obtained as the sum of four $2\Sigma(2J+1)e^{-\varepsilon_J/kT}$ terms, with different sets of ε_J values for the

[21] H. L. Johnston and M. K. Walker, *J. Amer. Chem. Soc.*, 1933, **55**, 172; *A.*, 1933, 229.

[22] *Idem*, *ibid.*, 1935, **57**, 682; *A.*, 690.

[23] W. Jevons, *op. cit.*, p. 126.

[24] H. L. Johnston and A. T. Chapman, *J. Amer. Chem. Soc.*, 1933, **55**, 153, 229.

A and B rotational levels of each constituent of the doublet.[25] The factor 2 is the nuclear-spin contribution, since i_s is $\frac{1}{2}$ for hydrogen, and zero for oxygen.

Since the cyanide radical has a $^2\Sigma$ ground term, there is no Λ-type doubling, although every rotational level is a duplet. The value of J for one set (F_1) is equal to $K + \frac{1}{2}$, and for the other (F_2) it is $K - \frac{1}{2}$, where K, the rotational quantum number, can have any integral value, including zero; when $K = 0$, however, the corresponding F_2 level is missing. The p values of the F_1 and F_2 series are, therefore, $2K + 2$ and $2K$, respectively, each being then multiplied by the nuclear-spin factor 3, since the spins of the carbon and nitrogen nuclei are 0 and 1, respectively. The complete rotational partition function [26] for this radical is consequently

$$3\sum_{K=0,1,2,3\ldots}(2K + 2)e^{-\epsilon_{K(F_1)}/kT} + 3\sum_{K=1,2,3,4\ldots}2Ke^{-\epsilon_{K(F_2)}/kT}$$

Energy Values.—In the early applications [27] of the partition function for the determination of thermodynamic constants, the energies of the rotational levels were calculated from the actual frequencies of the spectral lines of the molecules concerned, the lowest rotational level in the $v = 0$ vibrational band being taken as the zero point. Recent analyses of band spectra, however, have permitted the expression of the frequencies of the lines of a given electronic level, for diatomic molecules, in the form of equations of the type [28]

$$\nu = \nu_0 + \omega_e(v + \tfrac{1}{2}) - x\omega_e(v + \tfrac{1}{2})^2 \ldots + B_vJ(J + 1) + D_vJ^2(J + 1)^2 + F_vJ^3(J + 1)^3 \quad . \quad . \quad (18)$$

where ν_0 is the electronic frequency-separation, ω_e the equilibrium vibration frequency, x the anharmonic vibration constant, and v and J (sometimes K) are the vibrational and rotational quantum numbers, respectively. The factors B_v and D_v vary with the vibrational level according to the relationships

$$B_v = B_e - \alpha(v + \tfrac{1}{2}) + \gamma(v + \tfrac{1}{2})^2 \ldots$$
$$D_v = D_e + \beta(v + \tfrac{1}{2})^2 + \delta(v + \tfrac{1}{2})^4 \ldots$$

B_e, D_e, and α, β, γ, and δ being constants for the electronic level, which are determined from the observed spectral frequencies. The quantity F_v also depends on v, but as it is in any case very small, it may be assumed constant. The purpose of the correction factors is to allow for changes in the moment of inertia of the molecule in different vibrational levels, and for the interaction of vibrational and rotational energies. For a rigid molecule in which there is no interaction D_v and F_v are zero, and B_v is constant and equal to $h^2/8\pi^2I$, where I is the moment of inertia. By means of these equations the frequencies of all the rotational lines can be calculated and hence the *total internal energy,* including electronic and vibrational energy, of the corresponding levels can be determined; the value of ϵ to be used in the partition function Q is then obtained by subtracting the energy for the lowest level ($v = 0$, $J = 0$) in the ground state, *i.e.*, the zero-point energy, $(\frac{1}{2}\omega_e - \frac{1}{4}x\omega_e)hc$.* When spectroscopic measurements are relatively limited, it is often possible by means of the frequency equations to determine, with fair accuracy, the energies of levels giving rise to bands beyond the limit of actual experimental observation; such energies have frequently to be used in the calculation of thermodynamic quantities.

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[25] H. L. Johnston and D. H. Dawson, *J. Amer. Chem. Soc.*, 1933, **55**, 2744; *A.*, 1933, 1005.

[26] Cf. F. A. Jenkins, Y. K. Roots, and R. S. Mulliken, *Physical Rev.*, 1932, **39**, 16; *A.*, 1932, 145; see H. Zeise, *Z. Elektrochem.*, 1933, **39**, 899.

[27] H. C. Hicks and A. C. G. Mitchell, *loc. cit.*, ref. (4); W. F. Giauque and R. Wiebe, *J. Amer. Chem. Soc.*, 1928, **50**, 101; *A.*, 1928, 228.

[28] W. Jevons, *op. cit.*, Chap. II.

Summation.—In the determination of Q, the rotational portion, using the appropriate energies and statistical weights, is first determined by summing the series for all possible rotational levels (see above) in the $v = 0$ vibrational level, for the ground state of the molecule. The process is then repeated for the $v = 1, 2, 3$, etc., levels, as long as they contribute appreciably to the partition function. The same process is then carried out for every electronic state of relatively low energy separation, and the various sums added to give the complete state sum. Since the separations of successive rotational levels are relatively small, it is evident that, except at very low temperatures, such levels will contribute appreciably to the total partition function until high rotational quantum numbers are attained. With nitric oxide, for example, the rotational contribution becomes negligible only after 81 levels, in the $v = 0$ state, at 1000° Abs., and 168 and 200 levels must be included at 2000° and 3000° Abs., respectively.[24] It is evident, therefore, that the process of summation may become very tedious at high temperatures, where several vibrational, and possibly electronic, states must be included. Various methods have been employed for simplifying the labour involved: by means of appropriate frequency equations, of the type of equation (18), the internal energy is expressed in the form of asymptotic series of exponential terms, and summation is replaced by integration; provided the temperature is not too low, the error involved in the determination of Q is negligible. The method in its simplest form was first used for rigid diatomic molecules,[29] and was later modified [30] to allow for non-rigidity in molecules having $^1\Sigma$ ground terms. It permitted the determination of the rotational partition function for a given vibrational state by summing a small number of terms in a series : the calculation had to be repeated for each vibrational level contributing materially to the total sum. Since the evaluations of entropy and heat capacity require a knowledge of the first and second derivatives of Q [equations (6) and (8)], these have also been expressed as a similar series which can be summed quite readily.[31] If many vibrational levels have to be taken into account, then the summation is still laborious, although the work can be simplified by utilising the observation that the rotational function $Q_{\text{rot.}}$, and its derivatives $dQ_{\text{rot.}}/dT$ and $d^2Q_{\text{rot.}}/dT^2$, for one vibrational level v bear a constant ratio to the values for the $v + 1$ level.[31] Further developments [32] have eliminated even this summation, and have permitted the application of the mathematical methods to determine complete partition functions of $^2\Pi$ and $^3\Sigma$ diatomic molecules,[33] and even of polyatomic non-linear molecules (see below). By means of suitable tables, based on the formulæ derived, the labour involved in the calculation has been considerably diminished. These tables, and formulæ, apply only to unsymmetrical molecules in which there is no alternation in the statistical weights of odd and even levels, and they do not allow for nuclear spin : allowance can be made for both these factors, as will be seen later (p. 78).

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* The equation (18) for the frequency of spectral lines can be expressed in such a form as to give the required energy ϵ directly.

Approximation Methods.—If the different forms of internal energy of a molecule can be regarded as independent, the complete partition function can be taken as equal to the product of electronic, vibrational, and rotational functions, $Q_{\text{el.}}$, $Q_{\text{vib.}}$, and $Q_{\text{rot.}}$, respectively, where

$$Q_{\text{el.}} = \Sigma p_{\text{el.}} e^{-\epsilon_{\text{el.}}/kT} ; \quad Q_{\text{vib.}} = \Sigma p_{\text{vib.}} e^{-\epsilon_{\text{vib.}}/kT} ; \quad Q_{\text{rot.}} = \Sigma p_{\text{rot.}} e^{-\epsilon_{\text{rot.}}/kT}$$

and the complete partition function

$$Q = Q_{\text{el.}} \times Q_{\text{vib.}} \times Q_{\text{rot.}}$$

In evaluating the separate terms, $p_{\text{el.}}$ may be taken as equal to the multiplicity of the particular electronic state, provided the energy of separation of the multiplets is not large, and $\varepsilon_{\text{el.}}$, the corresponding energy of the level above the ground state, determined from the value of ν_0 in equation (18). In the $Q_{\text{vib.}}$ term, $p_{\text{vib.}}$ is always unity for a diatomic molecule; $\varepsilon_{\text{vib.}}$ may be taken as being the same in all electronic levels, and equal to $hc\omega_0 v$ above the zero-point energy, neglecting the anharmonicity constant, where ω_0 is the equilibrium frequency in the ground state. The vibrational partition function is thus given by the expression

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[29] H. P. Mulholland, *Proc. Camb. Phil. Soc.*, 1928, **24**, 280; G. B. B. M. Sutherland, *ibid.*, 1930, **26**, 402; *A.*, 1930, 1244.

[30] W. F. Giauque and R. Overstreet, *loc. cit.*, ref. (13); L. S. Kassel, *J. Chem. Physics*, 1933, **1**, 576; *A.*, 1934, 31.

[31] H. L. Johnston and C. O. Davis, *J. Amer. Chem. Soc.*, 1934, **56**, 271; *A.*, 1934, 354.

[32] A. R. Gordon and C. Barnes, *J. Chem. Physics*, 1933, **1**, 297; *A.*, 1934, 31; L. S. Kassel, *loc. cit.*, ref. (30); *Physical Rev.*, 1933, **43**, 364.

[33] A. R. Gordon and C. Barnes, *loc. cit.*; L. S. Kassel, *locc. cit.*; E. E. Witmer, *J. Chem. Physics*, 1934, **2**, 618; *A.*, 1934, 1165; see also C. Gregory, *Z. Physik*, 1932, **78**, 791; *A.*, 1933, 16.

$$Q_{\text{vib.}} = \sum_{v=0}^{\infty} e^{-hc\omega_0 v/kT} = (1 - e^{-hc\omega_0/kT})^{-1}$$

Since the rotational and vibrational energies are assumed independent, the molecule may be taken as rigid and the moments of inertia constant; the rotational energy of such a $^1\Sigma$ diatomic molecule may then be written $J(J + 1)h^2/8\pi^2 I$, and consequently

$$Q_{\text{rot.}} = \sum_{J=0}^{\infty}(2J + 1)e^{-\sigma J(J+1)}$$

where $\sigma = h^2/8\pi^2 IkT$. In this equation the nuclear-spin factor is neglected, and it is also assumed that the molecule is heteronuclear, so that there is no alternation in the p values for successive rotational levels. If σ is small, *i.e.*, for relatively high temperatures, and especially for molecules having small moments of inertia, the summation can be replaced by integration,[29, 34] with the result that $Q_{\text{rot.}} = 1/\sigma$. For molecules in other than $^1\Sigma$ states, analogous approximate values for the rotational function, applicable at appreciable temperatures, can be deduced; if necessary, the effect of Λ-type doubling must be included by means of a factor 2, the frequency separation being ignored. Allowance for multiplicity due to nuclear spin is made (p. 74) by multiplying $Q_{\text{rot.}}$ by $(2i_s + 1)(2i'_s + 1)$ for a heteronuclear molecule.

If the molecule has two identical atoms, the effect of nuclear spin should be obtained by multiplying the odd and even terms by $i_s(2i_s + 1)$ and $(i_s + 1)(2i_s + 1)$, as already explained (p. 73). In the summation of the $(2J + 1)e^{-\sigma J(J+1)}$ terms over all values of J from 0 to ∞, it can be shown that, provided σ be small, the sum of the terms for which J is even is equal to that for the terms with odd J values.[35] The inclusion of the nuclear-spin factor is consequently equivalent to multiplying the $Q_{\text{rot.}}$ obtained above by $(2i_s + 1)^2/2$; for hydrogen this correction factor is 2, for deuterium it is $\frac{9}{2}$, and for oxygen $\frac{1}{2}$. This last result is obviously in agreement with the fact that the alternate rotational levels of oxygen are missing, and the

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[34] L. S. Kassel, *J. Amer. Chem. Soc.*, **1933**, **55**, 1351; *A.*, **1933**, 561.

[35] See L. S. Kassel, *loc. cit.*, ref. (30).

others show no nuclear-spin degeneracy. For molecules of this type the approximate value of $Q_{\text{rot.}}$ becomes $1/2\sigma$: this result had been previously deduced by classical mechanics,[36] the factor 2, called the " symmetry number," representing the number of equivalent orientations in space which the molecule is able to occupy as a result of simple rotation.[37] Since the expression for entropy [equation (7)] involves $R \ln Q$, the correction for symmetry and for nuclear-spin degeneracy with a diatomic molecule is $2R \ln (2i_s + 1) - R \ln 2$; if $i_s = 0$, as for oxygen, this becomes $- R \ln 2$.

It should be noted that the equality of the odd and even terms in the $Q_{\text{rot.}}$ summation is only approached when σ is small : for most molecules, the temperature at which this occurs is quite low, but with *equilibrium* hydrogen and deuterium it is not the case. With these substances [38] it only applies when the ratio of ortho- to para-forms has attained the values of 3 : 1 and 1 : 2, respectively, and this is only the case at about 273° Abs. for hydrogen and at 200° Abs. for deuterium. For " normal " hydrogen and deuterium the approximations described are, of course, applicable. With other homopolar molecules possessing nuclear spin, the " normal " ratio of ortho- and para-states is reached at such low temperatures that under reasonable conditions the summation and correction factors considered above are adequate.

If the partition functions are required for the calculation of equilibrium constants, then provided the temperatures are such that the approximations discussed are valid, it is permissible to omit the nuclear-spin factor, both from atoms and molecules, although the " symmetry number " must be included.[39] Since nuclear spins are not always known, it is customary to quote entropy and $F^\circ - E_0^\circ$ values with the spin-multiplicity effect omitted, but with due allowance for symmetry; in fact, these allowances must be made if the entropy values from spectroscopic data are to be used in conjunction with others determined from thermal measurements. These entropies have been called " virtual " entropies,[40] and given the symbol S^* ; if absolute values are required, a factor $R \ln (2i_s + 1)$ must be added for every atom of spin i_s in the molecule.

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[36] Cf. P. Ehrenfest and V. Trkal, *loc. cit.*, ref. (1).

[37] For full discussion, see J. E. Mayer, S. Brunauer, and M. G. Mayer, *loc. cit.*, ref. (11).

[38] See W. F. Giauque, *loc. cit.*, ref. (12); H. L. Johnston and E. A. Long, *loc. cit.*, ref. (15).

[39] G. E. Gibson and W. Heitler, *Z. Physik*, 1928, **49**, 465; H. Ludloff, *ibid.*, 1929, **57**, 227; W. F. Giauque and R. Overstreet, *loc. cit.*, ref. (13); J. E. Mayer *et al.*, *loc. cit.*, ref. (11); see, however, H. Ludloff, *Z. Physik*, 1931, **68**, 433; *A.*, 1931, 675; D. S. Villars, *Physical Rev.*, 1931, **38**, 1563.

[40] *Idem*, *ibid.*, p. 1552; *A.*, 1932, 14; R. M. Badger and S.-C. Woo, *J. Amer. Chem. Soc.*, 1932, **54**, 3523; *A.*, 1932, 1205.

Isotope Effect.—For substances containing isotopic forms, accurate spectroscopic data are generally available only for the molecule containing the predominant isotope; the corresponding values for other forms can be readily calculated, however, by assuming the binding forces between atoms to be independent of their isotopic nature. In the determination of the entropy of the normal mixture the entropies of the separate forms are multiplied by their respective mol.-fractions, determined from the isotopic and chemical atomic weights, and the results are added, the entropy of mixing being included. Thermally determined entropies do not involve this factor, and for use in conjunction with these, for calculation of equilibrium constants, the entropy of mixing is omitted: if this is done, then in the appropriate instance it is necessary also to neglect the fact that the statistical weight of a heteronuclear molecule, *e.g.*, $Cl^{35}Cl^{37}$, is double that of the symmetrical molecules, $Cl^{35}Cl^{35}$ and $Cl^{37}Cl^{37}$. The same result, at least for chlorine, may be obtained in a simpler manner by treating the substance as a homonuclear molecule, each atom having an atomic weight 35·46, the energy at each level being obtained by giving the proper proportional weights to the corresponding levels for the three types of isotopic molecules; this effect is believed to be general and to apply to all analogous cases.[41] Hydrogen chloride may be treated as a mixture of definite amounts of HCl^{35} and HCl^{37}, although the entropy of mixing and the nuclear-spin effect must not be included if the results are to be used in conjunction with thermal values.

*Polyatomic Molecules.**—With such molecules precise calculations are very difficult, partly because the spectra are complex and difficult to analyse, and partly because of the labour involved in the evaluation of the partition function when three, or more, moments of inertia and several types of vibration have to be considered.[42] By replacing summation by integration and using methods of asymptotic expansion,[43] it has been possible to diminish the labour involved in obtaining the Q sum for relatively simple polyatomic molecules, *e.g.*, HCN, CO_2, N_2O, C_2H_2, H_2O, SO_2, CH_4, and CD_4, due allowance being made for anharmonicity and for stretching and interaction terms. In most cases, however, the simplification is made of treating the molecule as rigid and of assuming the different forms of energy to be independent : the complete partition function is then the product of the separate electronic, vibrational, and rotational functions. At relatively high temperatures the errors involved in these assumptions are generally small.

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[41] W. F. Giauque and R. Overstreet, *loc. cit.*, ref. (13); W. G. Brown, *ibid.*, 1932, **54**, 2394; *A.*, 1932, 906; A. R. Gordon and C. Barnes, *J. Physical Chem.*, 1932, **36**, 2292; *A.*, 1932, 997.

[42] F. Hund, *Z. Physik*, 1927, **43**, 805; *A.*, 1927, 809; W. Elert, *ibid.*, 1928, **51**, 6; *A.*, 1929, 11; D. S. Villars and G. Schultze, *Physical Rev.*, 1931, **38**, 998; *A.*, 1931, 1216; D. S. Villars, *ibid.*, p. 1552; *A.*, 1932, 14; D. P. MacDougall, *ibid.*, p. 2074; D. M. Dennison, *ibid.*, 1932, **41**, 304; *A.*, 1932, 982; A. Adel and D. M. Dennison, *ibid.*, 1933, **43**, 716; **44**, 99; *A.*, 1933, 661, 885; Dennison, *Rev. Mod. Physics*, 1931, **3**, 280; H. R. Nielsen, *Physical Rev.*, 1932, **40**, 445; T. E. Sterne, *ibid.*, 1932, **39**, 993; **42**, 556; *A.*, 1932, 566; 1933, 118; D. S. Villars, *Chem. Reviews*, 1932, **11**, 369; E. B. Wilson, *J. Chem. Physics*, 1935, **3**, 276; *A.*, 810.

* See report on "Spectroscopy," p. 53.

The classification of polyatomic molecules according to the electronic configuration of the ground state is only possible for a relatively limited number of substances which behave as quasi-diatomic; in other cases it is assumed that there is only one electronic ground level and that excited levels do not contribute to the total state sum. The electronic factor in the partition function is thus generally, unless there is direct evidence to the contrary, taken as unity.

A molecule containing n atoms has in general $3n - 6$ normal modes of vibration : for a linear molecule this is increased to $3n - 5$, and is decreased to $3n - 7$ for a molecule of the ethane type because of internal rotation. Of this total, $n - 1$ are stretching (valency), the others being bending (deformation) vibrations. If the energy of the vibrational levels [44] can be expressed in terms of a formula similar to the one used for diatomic molecules, it is sometimes possible to make a reasonably accurate estimate of the vibrational partition function.[45] For a complex molecule it is generally the practice to use for each type of vibration the approximate relationship obtained for a diatomic molecule, *viz.*, $Q_{\text{vib.}} = (1 - e^{-hc\omega_i/kT})^{-1}$: the vibrational function for the whole molecule is given by the *product* of these terms, one for every possible vibrational mode.[46] If any of the frequencies are degenerate, due allowance must be made in the product, the corresponding term being included for each component of the degenerate frequency. The vibrational terms affect the complete Q value to a relatively small extent, except at high temperatures;[47] *e.g.*, at 298° Abs. $Q_{\text{rot.}}$ for nitrous oxide is 496, whereas $Q_{\text{vib.}}$ is 1·1; the introduction of approximation methods and the use of uncertain frequencies consequently result in relatively small errors. The rotational factor is the more important, and this may best be considered under the headings of different types of molecules.

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[43] A. R. Gordon, *J. Chem. Physics*, 1934, **2**, 65; 1935, **3**, 259; *A.*, 1934, 355; 1935, 811; I. E. Viney, *Proc. Camb. Phil. Soc.*, 1933, **29**, 142, 407 (correction); *A.*, 1933, 206; L. S. Kassel, *locc. cit.*, ref. (30), (34); *J. Chem. Physics*, 1935, **3**, 115; *A.*, 437.

[44] Cf. D. M. Dennison, *Rev. Mod. Physics*, 1931, **3**, 280.

[45] L. S. Kassel, *J. Amer. Chem. Soc.*, 1934, **56**, 1838; *A.*, 1934, 1300; R. W. Blue and W. F. Giauque, *ibid.*, 1935, **57**, 991; *A.*, 924.

[46] See B. Topley and H. Eyring, *J. Chem. Physics*, 1934, **2**, 217; *A.*, 1934, 851; R. H. Crist and G. A. Dalin, *ibid.*, p. 735; *A.*, 1935, 33; E. Teller and B. Topley, *J.*, 1935, 876; *A.*, 1076.

Linear molecules (*e.g.*, HCN, N_2O, CO_2, C_2H_2). The rotational energy, at least in the lower vibrational levels, may be expressed by the same formula as for a diatomic molecule,[48] although this is not strictly accurate.[44, 49] The moments of inertia being relatively large, it is permissible to replace summation by integration, and the approximation already described (p. 78) may be used. For a molecule possessing symmetry, the appropriate symmetry factor s must be introduced, giving $Q_{\text{rot.}} = 1/s\sigma$, thus allowing for missing levels. The value of I required to calculate σ is generally obtained from spectroscopic data, although it may be evaluated from the interatomic dimensions if they are known. The result does not include the nuclear-spin factor, for which allowance need only be made if the Q is required to calculate absolute entropy.

Spherical rotator (*e.g.*, CH_4, CCl_4, but not CMe_4 because of free rotation). Molecules possessing tetrahedral symmetry may be treated as spherical rotators having three equal moments of inertia: the rotational energy may be expressed by the same equation as for a diatomic molecule. From quantum-mechanical considerations, it is sometimes possible to allow for the statistical weights of different rotational levels, but if missing levels and nuclear-spin effects are ignored, each level has a p value of $(2J + 1)^2$; replacing summation by integration,[50] then at appreciable temperatures $Q_{\text{rot.}} = \pi^{1/2}/s\sigma^{3/2}$. The term σ has the same significance as previously (p. 78), I being assumed constant, and s is the symmetry number,[51] *viz.*, 12 for CH_4 and CCl_4, which allows for missing levels. The nuclear-spin factor is not included.

Symmetrical top. Under this heading may be considered two types of molecule: (*a*) single pyramidal, *e.g.*, NH_3, $CHCl_3$, or (*b*) double pyramidal, *e.g.*, C_2H_6. In molecules of this nature, two of the three moments of inertia are identical, $I_A = I_B > I_C$. For the single-pyramid type the rotational energy, assuming a rigid molecule, may be written [52] in the form given on p. 55, where K can have a series of $2J + 1$ values, *viz.*, $J, J - 1, \ldots, 0, \ldots -J + 1, -J$, for every value of J. The multiplicity of each rotational level is $2J + 1$, but owing to the introduction of K each level is $(2J + 1)$-fold degenerate. The application of the usual approximation methods [53] leads to $Q_{\text{rot.}} = \pi^{1/2}/s\sigma_{\text{A}}\sigma_{\text{C}}^{1/2}$, where σ_{A} and σ_{C} involve I_{A} and I_{C}, respectively. Complete analysis, with full allowance for statistical weights, etc., gives results very little different.

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[47] R. M. Badger and S.-C. Woo, *loc. cit.*, ref. (40), p. 3527.

[48] R. M. Badger and S.-C. Woo, *loc. cit.*, ref. (40).

[49] L. S. Kassel, *loc. cit.*, ref. (45).

[50] H. P. Mulholland, *loc. cit.*, ref. (29); L. S. Kassel, *loc. cit.*, ref. (34).

[51] See J. E. Mayer *et al.*, *loc. cit.*, ref. (11); A. R. Gordon and C. Barnes, *J. Physical Chem.*, 1932, **36**, 2601; *A.*, 1932, 1203.

For an ethane-like top, the rotational-energy equation is similar to that for the single pyramidal molecule, another term involving K' equal to $K \pm 2n$, where n is an integer, being included; [54] the approximate value [55] of $Q_{\text{rot.}}$ is then found to be $\pi/s\sigma_{\text{A}}\sigma_{\text{C}}$.

Asymmetrical top. For the general case in which the molecule is non-linear and has three different moments of inertia, the rotational energy cannot be expressed by a simple formula : the energies of the lower levels may be represented by a complex relationship [56] which has been actually used to calculate Q for the water molecule.[57] A satisfactory approximation,[53] at appreciable temperatures, assuming a rigid molecule, is obtained by substituting $I_{\text{A}}I_{\text{B}}$ for I_{A}^2 in the equation for a pyramidal molecule, thus $Q_{\text{rot.}} = (\pi/\sigma_{\text{A}}\sigma_{\text{B}}\sigma_{\text{C}})^{1/2}/s$. For a planar molecule, *e.g.*, H_2O or C_6H_6, $I_{\text{A}} + I_{\text{B}} = I_{\text{C}}$; for H_2O, $s = 2$; for C_6H_6, $s = 12$; and for *cyclo*hexene, $s = 2$, since it is non-planar.

Complex Molecules.—By analogy with the formulæ already given, it has been deduced [58] that for a molecule with several rotating parts

$$Q_{\text{rot.}} = \frac{1}{s\pi}\left\{\frac{8\pi^3(I_{\text{A}}^aI_{\text{B}}^bI_{\text{C}}^c\ \ldots\ )^{1/n}kT}{k^2}\right\}^{n/2}$$

$I_{\text{A}}, I_{\text{B}}, I_{\text{C}} \ldots$ being the moments of inertia of the molecule and of its independently rotating parts; $a, b, c \ldots$ are the rotational degrees of freedom associated with the corresponding moments of inertia, their sum being equal to n, the total number of rotational degrees of freedom; and s is the symmetry number, defined as the number of indistinguishable permutations produced by rotation of the molecule or of its parts. This relationship has been applied to calculate the entropies of methyl alcohol, methyl ether, toluene, acetone, *iso*butane, β-methyl-Δ^{β}-butene ($CMe_2{:}CHMe$), and *neo*pentane. The problem of complex molecules has also been examined from a more fundamental point of view [59] which appears to have considerable promise, especially in its application to normal paraffin hydrocarbons.[60]

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[52] F. Reiche, *Z. Physik*, 1926, **39**, 444; J. E. Mayer *et al.*, *loc cit.*, ref. (11).

[53] L. S. Kassel, *loc. cit.*, ref. (34); A. R. Gordon, *loc. cit.*, ref. (43); for classical treatment, see A. Eucken, *Physikal. Z.*, 1929, **30**, 818.

[54] H. R. Nielsen, *loc. cit.*, ref. (42); J. E. Mayer *et. al.*, *loc. cit.*, ref. (11).

[55] *Idem, ibid.*

[56] H. A. Kramers and G. P. Ittmann, *Z. Physik*, 1930, **58**, 217; D. M. Dennison, *loc. cit.*, ref. (44).

[57] A. R. Gordon and C. Barnes, *J. Physical Chem.*, 1932, **36**, 1143; *A.*, 1932, 695.

[58] J. O. Halford, *J. Chem. Physics*, 1934, **2**, 694; *A.*, 1934, 1300.

Since in all the approximation methods the nuclear-spin factor has been neglected, the partition function should be multiplied by $2i_s + 1$ for every nucleus if absolute entropies are required; for the calculation of dissociation constants or for combination with calorimetric data this correction should not be applied.

Applications.—The methods outlined above have been used in the calculation of thermodynamic functions, *e.g.*, entropy, heat capacity, and the free-energy function, $(F^{\circ} - E_0^{\circ})/T$, for the following molecules: [61] hydrogen,[62] hydrogen deuteride (HD),[63] deuterium,[64] oxygen,[65] ozone,[66] hydroxyl radical,[67] water,[68] methane,[69] ethylene,[70] acetylene,[71] ethane,[72] benzene,[73] *cyclo*hexene,[73] nitrogen,[74] ammonia,[75] nitric oxide,[76] nitrous oxide,[77] hydrogen cyanide,[78] sulphur (S_2),[79] hydrogen sulphide,[80] sulphur dioxide,[81] carbon disulphide and oxysulphide,[81a] sulphur monoxide (SO),[82] chlorine,[83] hydrogen chloride,[84] deuterium chloride,[85] bromine,[86] hydrogen bromide,[87] iodine,[88] hydrogen iodide,[89] deuterium iodide,[90] iodine monochloride,[91] carbon monoxide,[92] carbon dioxide,[93] chloromethanes,[94] the tetrachlorides of carbon, silicon, titanium, and tin,[95] arsenic and phosphorus trichlorides,[96] arsenic [96] and phosphorus [97] trifluorides, phosphine,[97] sulphur hexafluoride,[98] nickel carbonyl,[99] methyl alcohol, dimethyl ether, acetone and various hydrocarbons.[59]

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[59] M. L. Eidinoff and J. G. Aston, *J. Chem. Physics*, 1935, **3**, 379; *A.*, 1064.

[60] L. S. Kassel, private communication.

[61] For atoms, see refs. (12)—(15).

[62] D. M. Dennison, *Proc. Roy. Soc.*, 1927, [*A*], **115**, 483; *A.*, 1927, 817; R. H. Fowler, *ibid.*, 1928, [*A*], **118**, 52; *A.*, 1928, 469; T. E. Sterne, *ibid.*, 1931, [*A*], **130**, 367; **133**, 303; *A.*, 1931, 295, 1222; F. Hund, *Z. Physik*, 1927, **42**, 93; *A.*, 1927, 495; S. Däumichen, *ibid.*, 1930, **62**, 414; *A.*, 1930, 982; W. F. Giauque, *loc. cit.*, ref. (12); C. O. Davis and H. L. Johnston, *ibid.*, 1934, **56**, 1045; *A.*, 1934, 722; A. R. Gordon and C. Barnes, *J. Physical Chem.*, 1932, **36**, 1143; *A.*, 1932, 695; see also R. H. Fowler and T. E. Sterne, *Rev. Mod. Physics*, 1932, **4**, 635.

[63] H. C. Urey and D. Rittenberg, *loc. cit.*, ref. (19).

[64] *Idem, ibid.*; H. L. Johnston and E. A. Long, *loc. cit.*, ref. (15); H. Motz and F. Patat, *Monatsh.*, 1934, **64**, 17; *A.*, 1934, 480; K. Clusius and E. Bartholomé, *Z. Elektrochem.*, 1934, **40**, 524; *A.*, 1934, 951; *Z. physikal. Chem.*, 1935, [*B*], **30**, 258.

[65] W. F. Giauque and H. L. Johnston, *J. Amer. Chem. Soc.*, 1929, **51**, 2300; *A.*, 1929, 1137; H. L. Johnston and M. K. Walker, *loc. cit.*, ref. (21); *ibid.*, 1935, **57**, 682; *A.*, 690; B. Lewis and G. von Elbe, *ibid.*, 1933, **55**, 511; 1935, **57**, 1399; *A.*, 1933, 343, 1198; A. R. Gordon and C. Barnes, *J. Physical Chem.*, 1932, **36**, 2292; *A.*, 1932, 997.

[66] L. S. Kassel, *J. Chem. Physics*, 1933, **1**, 414; *A.*, 1934, 30.

[67] H. L. Johnston and D. H. Dawson, *J. Amer. Chem. Soc.*, 1933, **55**, 2744; *A.*, 1933, 1005.

[68] A. R. Gordon and C. Barnes, *loc. cit.*, ref. (62); A. R. Gordon, *J. Chem. Physics*, 1933, **1**, 308; 1934, **2**, 65, 549; *A.*, 1934, 30, 355, 1070.

[69] W. F. Giauque, R. W. Blue, and R. Overstreet, *Physical Rev.*, 1931, **38**, 196; D. S. Villars and G. Schultze, *loc. cit.*, ref. (42); D. S. Villars, *loc. cit.*, ref. (42); D. P. MacDougall, *loc. cit.*, ref. (42); T. E. Sterne, *ibid.*, 1932, **42**, 556; *A.*, 1933, 118; L. S. Kassel, *loc. cit.*, ref. (34); A. R. Gordon and C. Barnes, *J. Physical Chem.*, 1932, **36**, 2601; *A.*, 1932, 1203; R. D. Vold, *J. Amer. Chem. Soc.*, 1935, **57**, 1192; *A.*, 1064.

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[70] L. S. Kassel, *loc. cit.*, ref. (34); H. A. Smith and W. E. Vaughan, *J. Chem. Physics*, 1935, **3**, 341; *A.*, 934; A. V. Frost, *J. Gen. Chem. Russia*, 1934, **4**, 124; *A.*, 1934, 843.

[71] L. S. Kassel, *loc. cit.*, ref. (34); J. E. Mayer *et al.*, *loc. cit.*, ref. (11); A. R. Gordon, *J. Chem. Physics*, 1935, **3**, 259; *A.*, 811.

[72] H. A. Smith and W. E. Vaughan, *loc. cit.*, ref. (70); J. E. Mayer *et al.*, *loc. cit.*, ref. (11); A. V. Frost, *loc. cit.*, ref. (70).

[73] J. E. Mayer *et al.*, *loc. cit.*, ref. (11); V. Deitz and D. H. Andrews, *ibid.*, 1933, **1**, 62; *A.*, 1933, 212.

[74] W. F. Giauque and J. O. Clayton, *loc. cit.*, ref. (15); H. L. Johnston and C. O. Davis, *loc. cit.*, ref. (31).

[75] W. F. Giauque *et al.*, *loc. cit.*, ref. (69); D. S. Villars, *loc. cit.*, ref. (69); D. P. MacDougall, *loc. cit.*, ref. (69); T. E. Sterne, *Physical Rev.*, 1932, **39**, 993; *A.*, 1932, 566; W. M. D. Bryant, *J. Amer. Chem. Soc.*, 1931, **53**, 3014; *A.*, 1931, 1127.

[76] H. L. Johnston and W. F. Giauque, *J. Amer. Chem. Soc.*, 1929, **51**, 3194; *A.*, 1930, 24; H. L. Johnston and A. T. Chapman, *ibid.*, 1933, **55**, 153, 5073 (correction); *A.*, 1933, 229; R. W. Blue and W. F. Giauque, *loc. cit.*, ref. (45); A. R. Gordon and C. Barnes, *loc. cit.*, ref. (32); E. E. Witmer, *J. Amer. Chem. Soc.*, 1934, **56**, 2229; *A.*, 1935, 21.

[77] R. M. Badger and S.-C. Woo, *loc. cit.*, ref. (40); W. H. Rodebush, *Physical Rev.*, 1932, **40**, 113; R. W. Blue and W. F. Giauque, *loc. cit.*, ref. (45); L. S. Kassel, *loc. cit.*, ref. (45); A. R. Gordon, *loc. cit.*, ref. (71).

[78] R. M. Badger and S.-C. Woo, *loc. cit.*, ref. (40); A. R. Gordon, *loc. cit.*, ref. (71).

[79] C. W. Montgomery and L. S. Kassel, *loc. cit.*, ref. (15); P. C. Cross, *J. Chem. Physics*, 1935, **3**, 168; *A.*, 569; I. N. Godnev, *Physikal. Z. Sovietunion*, 1935, **7**, 442; *A.*, 1312.

[80] P. C. Cross, *loc. cit.*, ref. (79).

[81] A. R. Gordon, *J. Chem. Physics*, 1935, **3**, 367; *A.*, 1204; P. C. Cross, *ibid.*, p. 825.

[81a] P. C. Cross, *loc. cit.*

[82] C. W. Montgomery and L. S. Kassel, *loc. cit.*, ref. (15).

[83] W. F. Giauque and R. Overstreet, *loc. cit.*, ref. (13); T. E. Sterne, *Proc. Roy. Soc.*, 1931, [*A*], **131**, 339; *A.*, 1931, 674; A. R. Gordon and C. Barnes, *loc. cit.*, refs. (32), (65); H. M. Spencer and J. L. Justice, *J. Amer. Chem. Soc.*, 1934, **56**, 2311; *A.*, 1935, 21.

[84] W. F. Giauque and R. Wiebe, *loc. cit.*, ref. (27); E. Hutchisson, *ibid.*, 1928, **50**, 1895; *A.*, 1928, 941; W. F. Giauque and R. Overstreet, *loc. cit.*, ref. (13); T. E. Sterne, *Proc. Roy. Soc.*, 1931, [*A*], **133**, 303; *A.*, 1931, 1222; H. M. Spencer and J. L. Justice, *loc. cit.*, ref. (83); A. R. Gordon and C. Barnes, *locc. cit.*, refs. (32), (65).

[85] H. C. Urey and D. Rittenberg, *loc. cit.*, ref. (19).

[86] A. R. Gordon and C. Barnes, *loc. cit.*, ref. (32); *J. Chem. Physics*, 1933, **1**, 692; *A.*, 1934, 30; W. G. Brown, *J. Amer. Chem. Soc.*, 1932, **54**, 2394; *A.*, 1932, 906.

Equilibrium constants [1] have been evaluated for the following reactions : $H_2 \rightleftharpoons 2H$;[2] $D_2 \rightleftharpoons 2D$;[3] $HD \rightleftharpoons H + D$;[4] $2HD \rightleftharpoons H_2 + D_2$;[4] $O_2 \rightleftharpoons 2O$;[5] $O_3 \rightleftharpoons O_2 + O$;[6] $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$;[7] $H_2O \rightleftharpoons \frac{1}{2}H_2 + OH$;[7] $H_2O + D_2O \rightleftharpoons 2HDO$;[8] $HDO + H_2 \rightleftharpoons H_2O + D_2$;[9] $D_2O + H_2 \rightleftharpoons H_2O + D_2$;[10] N_2

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[87] W. F. Giauque and R. Wiebe, *J. Amer. Chem. Soc.*, 1928, **50**, 2193; *A.*, 1928, 1083; A. R. Gordon and C. Barnes, *loc. cit.*, ref. (32).

[88] W. F. Giauque, *ibid.*, 1931, **53**, 507; *A.*, 1931, 429.

[89] W. F. Giauque and R. Wiebe, *ibid.*, 1929, **51**, 1441; *A.*, 1933, 755.

[90] H. C. Urey and D. Rittenberg, *loc. cit.*, ref. (19).

[91] J. M. McMorris and D. M. Yost, *ibid.*, 1932, **54**, 2247; *A.*, 1932, 906.

[92] J. O. Clayton and W. F. Giauque, *ibid.*, 1932, **56**, 2610; 1933, **57**, 5071 (correction); *A.*, 1932, 906; L. S. Kassel, *J. Chem. Physics*, 1933, **1**, 576; *A.*, 1934, 31; H. L. Johnston and C. O. Davis, *loc. cit.*, ref. (31); A. R. Gordon and C. Barnes, *loc. cit.*, ref. (32).

[93] R. M. Badger and S.-C. Woo, *loc. cit.*, ref. (40); L. S. Kassel, *loc. cit.*, ref. (45); H. M. Spencer and J. L. Justice, *loc. cit.*, ref. (83); A. R. Gordon, *J. Chem. Physics*, 1933, **1**, 308; *A.*, 1934, 30.

[94] R. D. Vold, *loc. cit.*, ref. (69).

[95] D. M. Yost and C. Blair, *J. Amer. Chem. Soc.*, 1933, **55**, 2610; *A.*, 1933, 784.

[96] D. M. Yost and J. E. Sherborne, *J. Chem. Physics*, 1934, **2**, 125; *A.*, 1934, 473.

[97] D. M. Yost and T. F. Anderson, *ibid.*, p. 624; *A.*, 1934, 1289.

[98] D. M. Yost, C. C. Steffens, and S. T. Gross, *ibid.*, p. 311; *A.*, 1934, 830.

[99] A. B. F. Duncan and J. W. Murray, *ibid.*, p. 636; *A.*, 1934, 1289.

[1] For tabulated summaries, see H. Zeise, *Z. Elektrochem.*, 1934, **40**, 885; B. Lewis and G. von Elbe, *J. Amer. Chem. Soc.*, 1935, **57**, 612.

[2] W. F. Giauque, *loc. cit.*, ref. (12); re-calculated by H. Zeise, *loc. cit.*, ref. (1).

[3] H. L. Johnston and E. A. Long, *loc. cit.*, ref. (15); *ibid.*, 1934, **56**, 710 (correction).

[4] H. C. Urey and D. Rittenberg, *loc. cit.*, ref. (19); F. Patat and H. Hoch, *Monatsh.*, 1934, **64**, 229; *A.*, 1934, 1153.

[5] H. L. Johnston and M. K. Walker, *loc. cit.*, ref. (14); G. von Elbe and B. Lewis, *loc. cit.*, ref. (14).

[6] L. S. Kassel, *J. Chem. Physics*, 1933, **1**, 414; *A.*, 1934, 30.

[7] A. R. Gordon, *loc. cit.*, ref. (93).

[8] B. Topley and H. Eyring, *loc. cit.*, ref. (46).

[9] R. H. Crist and G. A. Dalin, *ibid.*, 1934, **2**, 442, 548 (correction); *A.*, 1934, 962, 1070; T. Förster, *Z. physikal. Chem.*, 1934, **27**, [*B*], 1; *A.*, 1935, 33; see also, L. Farkas and A. Farkas, *Trans. Faraday Soc.*, 1934, **30**, 1071; *A.*, 1935, 33.

[10] B. Topley and H. Eyring, *loc. cit.*, ref. (46); R. H. Crist and G. A. Dalin, *loc. cit.*, ref. (46).

$\rightleftharpoons 2N$;[11] $NO \rightleftharpoons N + O$;[12] $NO \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2$;[11] $N_2O \rightleftharpoons N_2 + \frac{1}{2}O_2$;[13] $C + CO_2 \rightleftharpoons 2CO$;[13, 14] $2CO_2 \rightleftharpoons 2CO + O_2$;[13] $CO \rightleftharpoons C + \frac{1}{2}O_2$;[15] $CO_2 + H_2 \rightleftharpoons CO + H_2O$;[13, 16] $C + 2H_2 \rightleftharpoons CH_4$;[17] $2C + 2H_2 \rightleftharpoons C_2H_4$;[17] $2C + H_2 \rightleftharpoons C_2H_2$;[18] $C_2H_4 + H_2 \rightleftharpoons C_2H_6$;[19] $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$;[20] $Cl_2 \rightleftharpoons 2Cl$;[21] $HCl \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}Cl_2$;[21] $Br_2 \rightleftharpoons 2Br$;[22] $HBr \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}Br_2$;[22] $I_2 \rightleftharpoons 2I$;[23] $HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$;[24] $IBr \rightleftharpoons \frac{1}{2}I_2 + \frac{1}{2}Br$;[25] $ICl \rightleftharpoons \frac{1}{2}I_2 + \frac{1}{2}Cl_2$;[26] $H_2 + 2DCl \rightleftharpoons D_2 + 2HCl$;[27] $H_2 + 2DI \rightleftharpoons D_2 + 2HI$;[27] $2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2$;[28] $P_2 \rightleftharpoons 2P$;[29] $S_2 \rightleftharpoons 2S$;[82] $SO \rightleftharpoons \frac{1}{2}S_2 + \frac{1}{2}O_2$;[82] $SO_2 \rightleftharpoons \frac{1}{2}S_2 + O_2$;[30] $SO_2 \rightleftharpoons SO + \frac{1}{2}O_2$;[30] $3H_2 + SO_2 \rightleftharpoons H_2S + 2H_2O$; $2CO_2 + \frac{1}{2}S_2 \rightleftharpoons 2CO + SO_2$; $CO_2 + H_2S \rightleftharpoons COS + H_2O$; $COS + H_2S \rightleftharpoons CS_2 + H_2O$; $CO + \frac{1}{2}S_2 \rightleftharpoons COS$; $2COS \rightleftharpoons CO_2 + CS_2$; $CS_2 \rightleftharpoons C + S_2$;[81a] and various interchange reactions involving the isotopes of lithium, carbon, oxygen, nitrogen, chlorine, and bromine.[31]

Discrepancies.—In general, there is excellent agreement between thermodynamic functions calculated from spectroscopic data and the values obtained by direct experiment: in a few cases there are, however, outstanding discrepancies which require consideration. The statistical entropy of hydrogen is 33·98 units, including the nuclear-spin contribution, compared with the accurate thermal value of 29·6—29·7 at 298·1° Abs. :[32] there has been some controversy[33] over this difference, but it is now accepted as being due to the persistence of rotation in the solid,[34] so that the thermal method, based on the third-law assumption of zero entropy, is incorrect. The calculated error, 4·39 units, is in excellent agreement with the observed discrepancy of 4·3—4·4 units. The correct (virtual) entropy of hydrogen to be used in conjunction with the values for other substances is obtained by subtracting R ln 4, the nuclear-spin correction, from 33·98, giving 31·23 units. A similar difference exists between calculated and thermal entropies of deuterium, the values being 38·98 and 33·9, respectively :[35] this agrees excellently with the calculated discrepancy (5·09 units). The virtual entropy of D_2 is 38·98 − R ln 9 (the nuclear-spin effect), giving 34·62 units at 298·1° Abs. The calculated entropy of nitric oxide is about 0·75 greater than the thermal value :[36] since this difference is approximately $\frac{1}{2}R$ ln 2 it has been attributed to the presence of N_2O_2 in the solid, which exists either[36] in two forms with different coupling energies, or[37] in a single form possessing two different possible orientations distributed at random. For nitrous oxide the experimental value is 1·14 less than that obtained from spectroscopic data : if in the solid the nitrous oxide molecules could be oriented in a random manner either as NNO or ONN, the crystal would possess an entropy of 1·38 instead of zero. If the orientation were not completely random, the discrepancy might be somewhat less than this amount.[37] A discrepancy of the same order, 1·1 units, for carbon monoxide has been attributed to a similar random, possibly not complete, arrangement of CO and OC in the crystalline state.[38] There also appears to be some difference between the experimental and calculated entropies of water : this might well be due to the persistence of rotation in ice at temperatures as low as 10° Abs.[39] The disagreement between thermal and spectroscopic entropies of benzene has been ascribed to the possibility of deviation from flatness of the ring,[40] but similar differences have been observed for molecules the configurations of which are in no doubt.[41] These effects are probably due to incomplete knowledge of the vibrational modes of complex molecules. The uncertainty in treating the problem of free rotation of the methyl group in ethane may account for the calculated equilibrium constants for $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ being one-half the experimental values.[42] It must be emphasised in conclusion that, whenever detailed analysis of rotational and vibrational levels is possible and accurate spectroscopic data are available, the statistical thermodynamic constants are more reliable than those determined thermally by measurements based on the third law. S. G.

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[11] W. F. Giauque and J. O. Clayton, *loc. cit.*, ref. (15); recalculated by H. Zeise, *loc. cit.*, ref. (1) (p. 886).

[12] H. L. Johnston and A. T. Chapman, *loc. cit.*, ref. (76); recalculated by H. Zeise, *loc. cit.*, ref. (1) (p. 886).

[13] L. S. Kassel, *loc. cit.*, ref. (45).

[14] A. R. Gordon, *loc. cit.*, ref. (93); A. R. Gordon and C. Barnes, *loc. cit.*, ref. (69).

[15] J. O. Clayton and W. F. Giauque, *loc. cit.*, ref. (92).

[16] A. R. Gordon, *locc. cit.*, ref. (68); A. R. Gordon and C. Barnes, *loc. cit.*, ref. (62).

[17] L. S. Kassel, *loc. cit.*, ref. (34); A. R. Gordon and C. Barnes, *loc. cit.*, ref. (69).

[18] L. S. Kassel, *loc. cit.*, ref. (34).

[19] H. A. Smith and W. E. Vaughan, *loc. cit.*, ref. (70); A. V. Frost, *Compt. rend. Acad. Sci. U.R.S.S.*, 1933, **4**, 161; *A.*, 1934, 254; see also E. Teller and B. Topley, *loc. cit.*, ref. (46).

[20] A. R. Gordon and C. Barnes, *loc. cit.*, ref. (69).

[21] W. F. Giauque and R. Overstreet, *loc. cit.*, ref. (13).

[22] A. R. Gordon and C. Barnes, *J. Chem. Physics*, 1933, **1**, 692; *A.*, 1934, 30.

[23] G. E. Gibson and W. Heitler, *loc. cit.*, ref. (39); H. Zeise, *loc. cit.*, ref. (1) p. 887.

[24] H. Zeise, *loc. cit.*, ref. (1), p. 887.

[25] *Idem*, *Z. Elektrochem.*, 1935, **41**, 267; *A.*, 702.

[26] J. McMorris and D. M. Yost, *loc. cit.*, ref. (91); H. Zeise, *loc. cit.*, ref. (1), p. 888.

[27] H. C. Urey and D. Rittenberg, *loc. cit.*, ref. (19).

[28] A. R. Gordon and C. Barnes, *loc. cit.*, ref. (65).

[29] H. Zeise, *loc. cit.*, ref. (1), p. 888.

[30] A. R. Gordon, *J. Chem. Physics*, 1935, **3**, 336; *A.*, 1204.

[31] H. C. Urey and L. J. Greiff, *J. Amer. Chem. Soc.*, 1935, **57**, 321; *A.*, 446.

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[32] W. F. Giauque, *J. Amer. Chem. Soc.*, 1930, **52**, 4816; *A.*, 1931, 294.

[33] H. L. Johnston and W. F. Giauque, *ibid.*, 1928, **50**, 3221; *A.*, 1929, 138; R. H. Fowler, *loc. cit.*, ref. (62); R. H. Fowler and T. E. Sterne, *loc. cit.*, ref. (62); W. H. Rodebush, *Proc. Nat. Acad. Sci.*, 1929, **15**, 678; *A.*, 1929, 127; *Physical Rev.*, 1931, **37**, 221; D. MacGillavry, *ibid.*, 1930, **36**, 1398; *A.*, 1931, 31; W. F. Giauque, *ibid.*, p. 1592; *loc. cit.*, ref. (31); W. M. D. Bryant, *loc. cit.*, ref. (75).

[34] L. Pauling, *Physical Rev.*, 1930, **36**, 43; *A.*, 1930, 1357; see also R. H. Fowler, *Proc. Roy. Soc.*, 1935, [*A*], **151**, 1.

[35] K. Clusius and E. Bartholomé, *Z. physikal. Chem.*, 1935, **30**, [*B*], 258.

[36] H. L. Johnston and W. F. Giauque, *loc. cit.*, ref. (76).

[37] R. W. Blue and W. F. Giauque, *loc. cit.*, ref. (77).

[38] J. O. Clayton and W. F. Giauque, *loc. cit.*, ref. (92).

5. CHEMICAL KINETICS.

From the benefactions of the quantum theory to chemistry in general, the subject of reaction kinetics has received a rich share. The resulting new theory of chemical change incorporates the classical theory as a special case, and has the additional advantage of affording a more intimate glimpse into the actual mechanism of reaction. The distinction between the two theories may be illustrated by reference to bimolecular metatheses. The classical theory accepts the energy of activation (E) as a characteristic, experimentally ascertainable property of the reaction, and then proceeds to examine the frequency of collisions of critical violence.[1] The watchful eye of the theorist follows, as it were, the approach of reacting molecules until they come to grips, whereupon the eye is closed, to be opened again only when the chemical change is a *fait accompli* and the products of reaction are flying apart. The quantum theory, on the other hand, is not content with accepting E as a dynamic datum, but aims at evaluating it from the static properties of the reactants and resultants. The idea of collisional violence is maintained, but the watchful eye is kept wide open during the crash, in which old atomic allegiances are seen to be torn and new ones forged. The methods hitherto adopted for the *a priori* calculation of E and of other related terms are admittedly of an approximate character, yielding results which are only in partial agreement with experiment. The qualified arithmetical success of the quantum-mechanical theory is, however, more than counterbalanced by the general correctness of the physical hypotheses which make such calculations possible. For the purpose of the present report, some knowledge of the new theory is essential; current theoretical research subsumes it, and much of the experimental work is most conveniently discussed in its light.

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[39] W. F. Giauque and M. F. Ashley, *Physical Rev.*, 1933, **43**, 81; H. Zeise, *Z. Elektrochem.*, 1933, **39**, 905; A. R. Gordon, *J. Chem. Physics*, 1934, **2**, 65; *A.*, 1934, 355.

[40] V. Deitz and D. H. Andrews, *loc. cit.*, ref. (73).

[41] D. M. Yost and C. Blair, *loc. cit.*, ref. (95).

[42] H. A. Smith and W. E. Vaughan, *loc. cit.*, ref. (70).

[1] H. Goldschmidt, *Physikal. Z.*, 1909, **10**, 206; M. Trautz, *Z. anorg. Chem.*, 1916, **96**, 1.

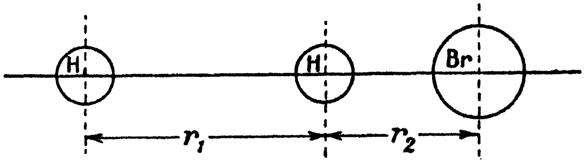
The Picture of Chemical Change Drawn by Quantum Mechanics.— We shall illustrate the method of H. Eyring and M. Polanyi [2] by setting ourselves the problem of evaluating the energy of activation of the reaction $Br + H_2 \longrightarrow HBr + H$, which M. Bodenstein has shown to be 17,700 calories. The perturbation theory of quantum mechanics yields the following simple expression [3] for the potential energy of a triatomic system, in terms of the Coulombic energies, A, B, and C, and of the exchange or resonance energies, α, β, and γ:

$$E = A + B + C + \{\tfrac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\alpha - \gamma)^2]\}^{\frac{1}{2}} \quad (1)$$

In general, the magnitude of the six separate contributions to the total energy is not known, but the quantities $(A + \alpha)$, $(B + \beta)$, and $(C + \gamma)$ can be directly found from the Morse functions of the relevant diatomic configurations. The evaluation of E thus requires a knowledge of the proportion of the total energy which is contributed by the Coulombic terms. The absence of a fixed or universal method of estimation and the approximate nature of the actual estimation are the first vulnerable points in the theory. The previously accepted value of 3·5% is certainly too low; and it is now believed that 14%, which is known to hold for the hydrogen molecule, is nearer the mark. Adopting it, we may rewrite equation (1) thus:

$$E = 0{\cdot}14\{(A+\alpha) + (B+\beta) + (C+\gamma)\} + 0{\cdot}61\{[(A+\alpha) - (B+\beta)]^2 + [(B+\beta) - (C+\gamma)]^2 + [(A+\alpha) - (C+\gamma)]^2\}^{\frac{1}{2}} \quad . \quad . \quad (2)$$

The theoretically justifiable step of considering only linear combinations of the three atoms, *e.g.*,



introduces an obvious simplification, enabling us to write

$$\left.\begin{aligned}(A + \alpha) &= D'_{H_2}[1 - e^{-a_{H_2}[r_1 - r_0(H_2)]}]^2\\(B + \beta) &= D'_{HBr}[1 - e^{-a_{HBr}[r_2 - r_0(HBr)]}]^2\\(C + \gamma) &= D'_{HBr}[1 - e^{-a_{HBr}[r_2 + r_1 - r_0(HBr)]}]^2\end{aligned}\right\} \quad . \quad . \quad (3)$$

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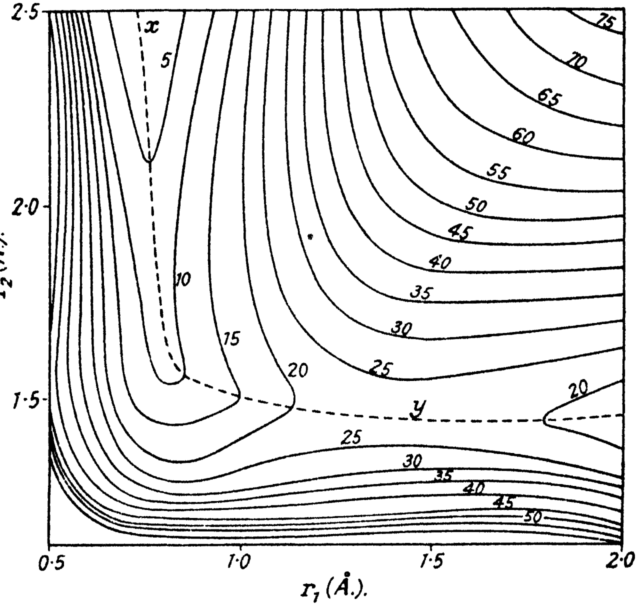
[2] *Z. physikal. Chem.*, 1931, [*B*], **12**, 279.

[3] W. Heitler and F. London, *Z. Physik*, 1927, **44**, 455.

where D' is the energy of dissociation (D) plus the zero-point energy ($\frac{1}{2}h\nu_0$). By combining equations (2) and (3), we obtain an expression for the potential energy of the triatomic system in terms of two spatial co-ordinates, r_1 and r_2 (Fig. 1).

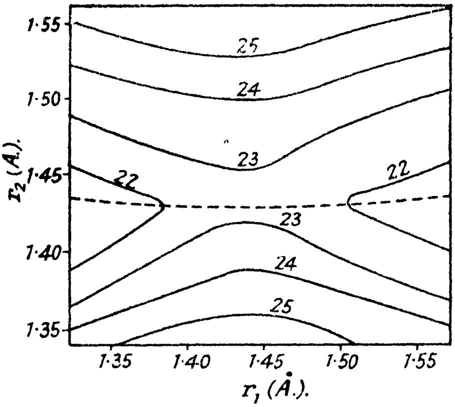
The initial system consists of a free bromine atom at an infinite distance away from a stable hydrogen molecule, and is represented by a point [$r_2 = \infty$; $r_1 = r_0(H_2)$; $E = D'_{H_2}$] in the top left-hand corner of Fig. 1. The final system corresponds to a free hydrogen atom, infinitely separated from a stable hydrogen bromide molecule, and is characterised by the point [$r_1 = \infty$; $r_2 = r_0(HBr)$; $E = D'_{HBr}$]. The passage of the system from its initial to its final state clearly corresponds to the occurrence of the chemical reaction $Br + HH \longrightarrow BrH + H$, for which the heat of reaction is simply $D'_{HH} - D'_{HBr}$. The easiest of an infinite number of such passages is that traced by the broken line. If we imagine ourselves to take the place of the representative point of the reacting system, we can gain a clearer view of what happens. Starting at x, we climb a gentle ascent southwards in a valley flanked by mountains, those on our right being the steeper. Round about the position y, there is a virtually horizontal walk, beyond which we descend into a second valley eastwards. The crux of the theory of Eyring and Polanyi is the identification of the height of the pass with the energy of

FIG. 1.



activation. The critically activated complex, represented by the point *y*, has certain definite probabilities of changing and of being formed in either of two ways: $H + HBr \rightleftarrows [H\text{---}H\text{---}Br] \rightleftarrows H_2 + Br$. From the magnified contour of the saddle region (Fig. 2), the complex is characterised by $r_1 = r_2 = 1{\cdot}43$ Å. and $E = 22{,}100$ calories. The identity of r_1 and r_2, though possibly accidental, fits in with the hypothesis of D. S. Villars[4] that E is the minimum energy of the system which is compatible with equal atomic separations. The discrepancy between the observed and calculated values of E is due partly to the approximate nature of London's equation, to the uncertainty about the Coulombic exchange ratio, and to the omission of statistical averaging. The energy-mountain model, in spite of its crudeness, is the rock upon which quantum-mechanical theories of chemical change are built. It is believed to depict, at least in broad outline, the essential features of the mechanism of those simple chemical reactions which proceed without electronic transitions. Such reactions are said to be adiabatic.[5]

FIG. 2.



General Considerations on the Potential-energy Mountain.—A helpful aspect of the present theory is the light which it throws on some of the obscure factors which determine the course of chemical change. Expressions similar to equation (1) have been derived[6] for systems consisting of more than three atoms. Eyring and Polanyi's comparison of the theoretical energies of activation of the two reactions $H_2 + o\text{-}H_2 \longrightarrow H_2 + p\text{-}H_2$ and $H + o\text{-}H_2 \longrightarrow H + p\text{-}H_2$ showed E to be smaller for the latter reaction, which should therefore, *ceteris paribus*, be the more likely to occur. The conclusion is in agreement with the actual mechanism established by A. Farkas.[7] A comparison of the calculated E's for the reactions $C_2H_4I_2 \longrightarrow C_2H_4 + I_2$ and $C_2H_4I_2 + I \longrightarrow C_2H_4 + I_2 + I$ revealed but a trifling difference; [8] hence the two reactions should occur concurrently, as is found to be the case.[9] The predominant, though not exclusive,[10] addition of bromine in the 1 : 4-positions of the butadiene molecule has received a similar explanation.[11] As the mechanism of each reaction had been established by experiment before theoretical computations were made, it is evident that the function of the theory in this direction has, up to the present, been one of interpretation rather than of prediction. Perhaps the suitable note to strike at this juncture is not lament at the inability to predict, but delight at the ability to interpret.

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[4] *J. Amer. Chem. Soc.*, 1930, **52**, 1773.

[5] F. London, Sommerfeld Festschrift, p. 104, Hirzel, Leipzig, 1928.

[6] F. London, *Z. Elektrochem.*, 1929, **35**, 552; J. H. van Vleck and A. Sherman, *Rev. Mod. Physics*, 1935, **7**, 167; H. Hellmann, *Acta Physico-chimica U.R.S.S.*, 1935, **1**, 913.

The velocity of chemical reaction is determined by the number of molecules which possess the necessary energy (E) and by the probability (G) per unit time that the activated molecules will suffer transformation. E is represented by the height of the col, and G by the probability that the representative point surmounts it. Our estimate of G depends on whether the process obeys the laws of classical or those of quantum mechanics. Consider a one-dimensional barrier with a height corresponding to E. According to classical mechanics, the chance that a freely moving particle will surmount it is independent of its shape; particles with energy W will always pass the top provided $W \geq E$, and will never pass it when $W < E$. According to quantum mechanics, the probability of transit is finite even when $W < E$, and amounts to certainty only as $W \longrightarrow \infty$. In principle, G can always be evaluated when the potential energy barrier has been expressed analytically.[12] By making assumptions about the shape of the barrier, expressions can be deduced [13] relating its permeability (G) with its height (E) and width. Numerical computations for barriers of plausible widths and heights[14] show that G approximates to the classical value except when the mass, temperature, and energy of activation are low. It is conceivable that certain reactions exist, the rate of which is governed by the quantum-mechanical transmission of a hydrogen atom or proton, rather than by the co-ordinated evolutions of a system of atoms. Bell[14] has shown that, adopting a barrier of the shape postulated by Eckart[13] for an athermic reaction with $E = 14{,}500$ calories and a width of 2 Å., G varies with T in such a way that the Arrhenius E would be only 6,300 calories. If the somewhat speculative computations approximate to the truth, large differences are to be expected between observed and theoretical values of E. However, the behaviour of reactions involving massive particles may confidently be regarded as classical ($G = 1$ when $W \geq E$), particularly when E is appreciable.

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[7] *Z. physikal. Chem.*, 1930, [*B*], **10**, 419.

[8] A. Sherman and C. E. Sun, *J. Amer. Chem. Soc.*, 1934, **56**, 1096.

[9] L. B. Arnold and G. B. Kistiakowsky, *J. Chem. Physics*, 1933, **1**, 166.

[10] G. B. Heisig and J. L. Wilson, *J. Amer. Chem. Soc.*, 1935, **57**, 859.

[11] H. Eyring, A. Sherman, and G. E. Kimball, *J. Chem. Physics*, 1933, **1**, 586.

[12] E. Wigner, *Z. physikal. Chem.*, 1933, [*B*], **19**, 203.

[13] D. G. Bourgin, *Proc. Nat. Acad. Sci.*, 1929, **15**, 357; R. M. Langer, *Physical Rev.*, 1929, **33**, 290; C. Eckart, *ibid.*, 1930, **35**, 1303; S. Roginsky and L. Rosenkewitch, *Z. physikal. Chem.*, 1930, [*B*], **10**, 47; E. Wigner, *Physical Rev.*, 1932, **40**, 749; C. Zener, *Proc. Roy. Soc.*, 1932, [*A*], **137**, 696.

Recent classical treatments of the passage of the representative point over the col[15] have been synthesised and elaborated into a theory of great attractiveness by H. Eyring,[16] who considers the critical complex to resemble a stable molecule in all respects except in the motion along the co-ordinate of decomposition. On account of the flatness of the saddle region, the motion in this degree of freedom is regarded as classical. The governing idea is that the passage over the col is associated with constancy in the number, but change in the nature, of the degrees of freedom. When, for example, two atoms A and B collide to form a complex A . . . B, from which the stable molecule AB will ultimately emerge, the six translational degrees of freedom (three for each atom) are converted into three degrees of translation of the complex A . . . B as a whole, two degrees of freedom of rotation, and—most important of all—one degree of freedom of translation of the atoms A and B within the complex, along the line of centres. The velocity of reaction is largely a function of the energy in this special degree of freedom. Quantitative developments have recourse to a general theorem in statistical mechanics[17] (see also p. 66) which relates the equilibrium constant (K), for unit volume, with the energy change (E_0) and the relevant partition functions (F) :

$$K = F_{AB} \, . \, e^{-E_0/RT} / F_A F_B \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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[14] R. B. Bell, *Proc. Roy. Soc.*, 1933, [*A*], **139**, 466; 1935, **148**, 241; C. E. H. Bawn and G. Odgen, *Trans. Faraday Soc.*, 1934, **30**, 432.

[15] E. Wigner and M. Polanyi, *Z. physikal. Chem.*, 1928, **139**, 439; H. Pelzer and E. Wigner, *ibid.*, 1932, [*B*], **15**, 445; O. K. Rice and H. Gershinowitz, *J. Chem. Physics*, 1934, **2**, 853; W. H. Rodebush, *ibid.*, 1933, **1**, 440; 1935, **3**, 242; M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875.

[16] *J. Chem. Physics*, 1935, **3**, 107.

[17] R. H. Fowler, " Statistical Mechanics," Chap. V, Cambridge, 1929.

The evaluation of F is in general a difficult matter, unless the motions are completely classical or completely quantised, and can be treated as virtually independent. In such cases, F factorises into $F_1F_2F_3 \ldots$ Extracting from F_{AB} the factor which takes account of the motion in the "co-ordinate of decomposition," and regarding this motion as one in a force-free field, we get :

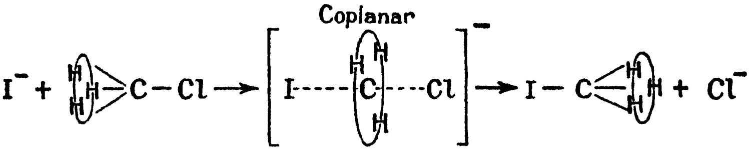
$$K = (F^*_{\mathrm{AB}}/F_{\mathrm{A}}F_{\mathrm{B}}) \,.\, e^{-E_0/RT} \,.\, \sqrt{2\pi mkT}/h$$

This expression gives the concentration of critical complexes at the col; multiplication by the average velocity $\sqrt{kT/2\pi m}$ of transit over the col gives us Eyring's general formula for the velocity of reaction :

$$k = (F^*_{\mathrm{AB}}/F_{\mathrm{A}}F_{\mathrm{B}}) \,.\, e^{-E_0/RT} \,.\, kT/h \quad . \quad . \quad . \quad . \quad (5)$$

In the particular example discussed here, $F^*_{\mathrm{AB}}/F_{\mathrm{A}} \,.\, F_{\mathrm{B}}$ becomes hZ/kT, where Z is the kinetic-theory value for the frequency of binary collisions. The classical equation for the velocity of simple bimolecular processes is thus deducible from somewhat novel premises. The theory has been helpful in elucidating several problems, including the rates of homologous unimolecular reactions in gases,[18] the negative temperature coefficient of the velocity of termolecular reactions,[19] and the variation of the steric factor with molecular complexity.[20] Its application to the problems of reactions in solution [21] makes appeal to the idea of entropy of activation.[22] Attention has been directed [23] to errors in the treatment of Wynne-Jones and Eyring.

An extension of the energy-mountain technique has shown the way to the calculation of the energy of activation of simple ionic reactions.[24] We shall illustrate the method by discussing the reaction $CH_3Cl + I' \longrightarrow CH_3I + Cl'$ in acetone solution. The charge on the attacking ion and the sign of the dipole predispose the approach to take place in the manner indicated :



During chemical change, therefore, the methyl chloride molecule is turned inside out, like an umbrella in a strong wind. This mechanism was dictated by the facts of the Walden inversion, and is consistent with Lowry's theorem that reaction takes place through the intermediate formation of a compound of higher symmetry. Direct support for it has recently been given by E. D. Hughes, F. Juliusberger, S. Masterman, B. Topley, and J. Weiss,[25] who have established experimentally the identity in the rate of inversion of *sec.*-octyl iodide and the rate with which the iodine atom is exchanged by its radioactive isotope. Ogg and Polanyi's expression for the potential energy of the reacting system may be written

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[18] O. K. Rice and H. Gershinowitz, *J. Chem. Physics*, 1935, **3**, 479.

[19] H. Gershinowitz and H. Eyring, *J. Amer. Chem. Soc.*, 1935, **57**, 985.

[20] C. E. H. Bawn, *Trans. Faraday Soc.*, 1935, **31**, 1536.

[21] W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Physics*, 1935, **3**, 492.

[22] F. G. Soper, Discussion on the Critical Increment, Chemical Society, 1931, p. 45; V. K. LaMer, *J. Chem. Physics*, 1933, **1**, 289.

[23] E. A. Moelwyn-Hughes, *ibid.*, in the press.

[24] R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604.

$$E_1 = S_{I^-} + D_{CH_3Cl}[1 - e^{-a(r_2 - r_0)}]^2 - \frac{\varepsilon\mu_{CH_3Cl}}{r_1^2} - \frac{\varepsilon^2\alpha}{2r_1^4} + b_0(I^-)e^{-r_1/p} \quad (6)$$

where r_1 is the separation of the iodine ion, and r_2 that of the chlorine atom, from the carbon atom, the polarisability of which is α. D_{CH_3Cl} is the heat of dissociation, and a and r_0 are the Morse constants for methyl chloride. The heat of solvation (S_{I^-}) of the iodine ion is computed from the constants (b_0 and p) of the repulsive field in crystals.[26] The use of a similar expression for the potential energy (E_2) of the product system allows an evaluation of the energy of activation (E). The result is 50% too high. Among the factors which are omitted from the treatment, one may mention the influence of the cation, the inclusion of which leads to a better value of E. Several conclusions of a qualitative, or at best a semi-quantitative, nature may be drawn from general considerations of the solid geometry of potential-energy models. Some of the problems relating to chemiluminescence,[27] prototropy [28] and exchange [29] have been approached from this angle. By a combination of the methods of Eyring and Polanyi [2] for non-polar systems with those of Ogg and Polanyi [24] for ionic systems, potential surfaces have been constructed for simple chemical changes where the reactants are of one kind and the resultants of another.[30]

Since the velocity coefficient (k) is usually proportional to $e^{-E/RT}$, any influence which lowers the energy of activation increases the velocity, and is thus positively catalytic. The introduction of an ion, a dipole, or a polarisable atom or molecule into an electrically neutral reacting system may, of course, increase or decrease the potential energy; and the height of the col may thereby be raised or lowered. In the former case, however, the disturbance merely makes possible an alternative mechanism which is less likely to occur than the undisturbed process, and may therefore be ignored. In the latter case, the disturbed mechanism is the more facile, and may replace the original one. Steps towards the formulation of a quantum-mechanical theory of catalysis have already been taken.[31]

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[25] *J.*, 1935, 1525.

[26] M. Born and J. E. Mayer, *Z. Physik*, 1932, **75**, 1.

[27] R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 1375.

[28] J. Horiuti and M. Polanyi, *Acta Physicochimica U.R.S.S.*, 1935, **2**, 505.

[29] R. A. Smith, *Proc. Camb. Phil. Soc.*, 1934, **30**, 508.

[30] A. G. Evans and M. G. Evans, *Trans. Faraday Soc.*, 1935, **31**, 1400.

It is a matter of interest to inquire into the possible connexion between the processes of activation, as the term is understood in chemical kinetics, and of the excitation of vibrational quanta. The study of the latter phenomenon is advancing rapidly.[32] Quantitative applications of the theories presuppose a precise knowledge of interatomic force-fields, and are possible only in very simple cases. Approximate solutions to the problem being accepted,[33] it can readily be shown, for example, that the chance of a hydrogen atom exciting the first vibrational quantum in the molecule of hydrogen bromide is negligible compared with the chance of chemical reaction, in all relevant collisions. On the other hand, with molecules of slightly higher complexity, the interchange of translatory and vibrational energy is of some importance. C. N. Hinshelwood,[34] co-ordinating the salient facts relating to the catalytic decomposition of gaseous aldehydes, ethers, and nitrous oxide, points out that the efficient catalysts (*e.g.*, iodine, halogen atoms, nitric oxide, and oxygen) possess the qualities (polarisability, free valency, odd electron, and magnetic moment) which according to classical theory favour specific energy transfers. The distinction thus appears to be due to the fact that, with an organic molecule, vibrational excitation occurs in bonds other than that which is eventually broken. Hinshelwood differentiates between a pre-activated molecule and a critically activated one : both possess the necessary energy, but the former lacks the appropriate internal distribution, while the latter possesses the necessary energy in the right spot, and will decompose in the course of the next complete vibration. Further reference will be made to the question of the internal redistribution of energy (see p. 108).

Atomic Reactions.—The study of reactions involving the simple replacement of one atom by another offers obvious advantages.

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[31] H. M. James and A. S. Coolidge, *J. Chem. Physics*, 1934, **2**, 811; A. E. Stearn, *J. Gen. Physiol.*, 1934, **18**, 171; A. A. Schuchowitzky, *Acta Physicochimica U.R.S.S.*, 1935, **1**, 901; R. M. Langer, *loc. cit.*, ref. (13).

[32] O. Schmidt, *Ann. Physik*, 1934, **21**, 241; H. O. Kneser, *Physikal. Z.*, 1934, **35**, 983; A. Eucken and R. Becker, *Z. physikal. Chem.*, 1934, [*B*], **27**, 219; J. E. Lennard-Jones and C. Strachan, *Proc. Roy. Soc.*, 1935, [*A*], **150**, 442.

[33] N. F. Mott and H. S. W. Massey, "The Theory of Atomic Collisions," p. 248, Oxford, 1933.

[34] *J.*, 1935, 1111.

A profitable approach to the investigation of any given chemical reaction, say $A + BC \longrightarrow AB + C$, is to examine it in conjunction with the sister reaction $A + BD \longrightarrow AB + D$, where C and D belong to the same family in the periodic table. Experience shows, however, that the study of the second reaction, instead of solving our first difficulties, very often introduces new ones. We find ourselves to be, in fact, very near the core of chemistry, which holds the secret of the specificity of the various forms of matter. An investigation of the twin reactions $A + BD_1 \longrightarrow AB + D_1$ and $A + BD_2 \longrightarrow AB + D_2$, where D_1 and D_2 are isotopes of the same element, should take us a stage nearer the goal, because isotopic specificity, for all chemical purposes, is confined to those properties which are directly related to their masses. Of these properties, zero-point energy is one of the most important.[35] From accurate spectroscopic values of ν, we have, for hydrogen, $E^\circ_{H_2} = 6{,}180$, and for deuterium, $E^\circ_{D_2} = 4{,}390$ calories per g.-mol., hence $E^\circ_{H_2} - E^\circ_{D_2} = 1{,}800$. The simplest known chemical reactions are (1) $H + H_2 \longrightarrow H_2 + H$; (2) $D + D_2 \longrightarrow D_2 + D$; (3) $H + D_2 \longrightarrow HD + D$; (4) $D + H_2 \longrightarrow DH + H$. Kinetic information about them is well-nigh complete.[36] The first two are the ortho-para conversion of hydrogen and deuterium; the second two are the significant steps in the reaction $H_2 + D_2 \rightleftharpoons 2HD$. The difference in velocity of reactions (1) and (2) is due to two factors, *viz.*, the difference in the collision frequencies and that in activation energies, which experiment shows to be about 500 calories. Now the energy of activation (E) is defined as the difference between the energy (E^*) of the activated state (HHH or DDD) and the energy (E°) of the initial state (H_2 or D_2); hence $E^*_{HHH} - E^*_{DDD} = (E^\circ_{H_2} - E^\circ_{D_2}) + (E_{H_2,H} - E_{D_2,D}) = 1{,}300$. This quantity is in agreement with the difference calculated for the energies of the systems HHH and DDD by making plausible assumptions about the force constants. Much of the existing literature has been considered in this light. The additional data for HHD, HDD, HDH, DHD, HHBr, DDBr, HHCl, etc., make it appear probable that critical complexes do, in fact, possess zero-point energy, and thus resemble stable molecules at least in one respect. The difference in E for the reactions $Na + HCl \longrightarrow NaCl + H$ (6,100 cals.) and $Na + DCl \longrightarrow NaCl + D$ (6,400 cals.) has been independently accounted for in the same way.[37] G. Schay has continued his work on the interaction of alkali atoms with molecules of halogen[38] and of mercury halides.[39] Except for a few details, the mechanism of reaction with potassium atoms is the same as that established with sodium.[40] The homogeneous reaction $K + I_2 \longrightarrow KI + I + q_1$ cals. is followed by a wall reaction $K + I \longrightarrow KI$ and by a second homogeneous reaction $K_2 + I \longrightarrow KI + K + q_2$ cals. The state of electronic excitation of the emergent potassium atom is governed largely by the magnitude of the heat effect q_2. The violet doublet is absent from the flame spectrum, in agreement with thermodynamic anticipation. From the temperature variation of one of the contributions to the total light intensity, the heat of dissociation of the reaction $K_2 \rightleftarrows 2K$ is found to be 18,700 cals. The rate and energy of activation for the reaction between sodium atoms and monohalogen derivatives of benzene have been measured and discussed,[41] as well as the reactions[42,43] $O + NO_2 \longrightarrow NO + O_2$ and $Br + Cl_2 \longrightarrow BrCl + Cl$.

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[35] (Frl.) E. Cremer and M. Polanyi, *Z. physikal. Chem.*, 1932, [*B*], **19**, 443.

[36] A. Farkas and L. Farkas, *Proc. Roy. Soc.*, 1935, [*A*], **152**, 124; A. Farkas, "Ortho-Hydrogen, Para-Hydrogen, and Heavy Hydrogen," Cambridge, 1935.

[37] C. E. H. Bawn and A. G. Evans, *Trans. Faraday Soc.*, 1935, **31**, 1392.

The actual union of two atoms to form a covalent molecule differs from the pictorial account discussed on p. 91, in that it requires the presence of a third atom or molecule to render the collision effective. The third partner may be a part of the wall of the reaction vessel, or a free atom or molecule in the gas. W. Steiner, whose earlier work[44] on the mechanism of ternary encounters has received new confirmation,[45] has elaborated his theory of the recombination of hydrogen atoms.[46] After allowing for the diffusion of hydrogen atoms to the wall, it appears that the reactions $H + H + \mathit{Molecule} \longrightarrow H_2 + \mathit{Molecule}$ and $H + H + \mathit{Atom} \longrightarrow H_2 + \mathit{Atom}$ have velocities in the approximate ratio of 9 : 10. Hydrogen atoms have been found to combine 1·36 times as fast as deuterium atoms, in agreement with our knowledge of the identity in diameters and force constants.[47] G. M. Schwab[48] has shown that every collision between a bromine atom from the gas phase and a similar atom adsorbed on the wall is effective.

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[38] E. Roth and G. Schay, *Z. physikal. Chem.*, 1935, [*B*], **28**, 323.

[39] I. Bereger and G. Schay, *ibid.*, p. 332.

[40] M. Kroesak and G. Schay, *ibid.*, 1932, [*B*], **19**, 344. References to still earlier work have been given by E. K. Rideal, *Ann. Reports*, 1928, and by C. N. Hinshelwood, *ibid.*, 1930, 1931.

[41] F. Fairbrother and E. Warhurst, *Trans. Faraday Soc.*, 1935, **31**, 987.

[42] M. L. Spielman and W. H. Rodebush, *J. Amer. Chem. Soc.*, 1935, **57**, 1474.

[43] G. Brauer and E. Victor, *Z. Elektrochem.*, 1935, **41**, 508.

[44] *Z. physikal. Chem.*, 1931, [*B*], **15**, 249.

[45] L. Farkas and H. Sachsse, *ibid.*, 1934, [*B*], **27**, 111; G. A. Cook and J. R. Bates, *J. Amer. Chem. Soc.*, 1935, **57**, 1775.

[46] W. Steiner, *Trans. Faraday Soc.*, 1935, **31**, 623, 962.

[47] I. Amdur, *J. Amer. Chem. Soc.*, 1935, **57**, 856.

[48] *Z. physikal. Chem.*, 1934, [*B*], **27**, 452. See also E. Rabinowitch and H. L. Lehmann, *Trans. Faraday Soc.*, 1935, **31**, 689.

As a matter of pure nomenclature, it may be pointed out that the term " exchange reaction " is being accepted for changes involving the replacement of an atom by one of its isotopes. The mechanism, as we have seen, is usually an atomic one.

More Complicated Reactions in the Gaseous Phase.—The repetition—perhaps inevitable—of some of the key experiments has consolidated the territories gained during the last decade in this domain. A reinvestigation [49] of the reaction $CH_3{\cdot}CHO \longrightarrow CH_4 + CO$ under the original conditions yields no evidence that it is appreciably heterogeneous, as is the case at lower temperatures [50] or that it depends upon a chain mechanism. It also appears [51] that the stationary concentration of hydrogen atoms is too low to maintain the type of chain mechanism mooted by F. O. Rice and K. F. Herzfeld.[52] The catalytic influence of oxygen and of two oxides of nitrogen on this reaction has been studied.[53] The decomposition of nitrous oxide, examined under pressures amounting to 40 atmospheres,[54] confirms the conclusions of F. F. Musgrave and C. N. Hinshelwood.[55] For both these reactions, the apparent E increases as the pressure is raised. The rôle of keten as the intermediate compound in the unimolecular decomposition of acetone has been quantitatively studied; again, there is evidence for composite activation and for the absence of long chains.[56] The thermal decomposition of ozone has been the subject of repeated investigation [57] and discussion.[58] Azomethane explodes at temperatures slightly higher than those at which H. C. Ramsperger measured the quiet unimolecular decomposition.[59] The study of the formation of hydrogen sulphide from its elements continues to offer difficulties, but the rôle played by sulphur atoms is becoming clearer.[60] The reaction between hydrogen and oxygen attracts unabated attention. The influence thereon of replacing hydrogen by deuterium,[61] of salt-coating the walls,[62] of passing electric discharges,[63] of introducing tetraethyl-lead,[64] and of the presence of a palladium catalyst[65] have all been examined. Recent values of the lower explosion limit[66] are somewhat lower than those found originally. The lower explosion limit for the oxidation of phosphine has been re-examined under a wide variety of conditions by S. C. Gray and H. W. Melville,[67] whose results, along with recalculated values for eight other reactions, confirm the accepted theory. New data on the lower explosion limit for the oxidation of carbonyl sulphide and of silane have been published by H. Gutschmidt and K. Clusius.[67a]

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[49] C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1935, [*A*], **149**, 355; M. Letort, *Compt. rend.*, 1935, **200**, 312.

[50] M. W. Travers, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 284; *Nature*, 1935, **135**, 511.

[51] F. Patat and H. Sachsse, *Naturwiss.*, 1935, **23**, 247.

[52] *J. Amer. Chem. Soc.*, 1934, **56**, 284.

[53] F. H. Verhoek, *Trans. Faraday Soc.*, 1935, **31**, 1521; E. W. R. Steacie and R. D. Macdonald, *Canadian J. Res.*, 1935, **12**, 711.

[54] E. Hunter, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 386. [55] *Ibid.*, 1932, **135**, 23.

[56] C. A. Winkler and C. N. Hinshelwood, *ibid.*, 1935, [*A*], **149**, 340.

[57] M. Ritchie, *ibid.*, 1934, [*A*], **146**, 848.

[58] H. J. Schumacher, *ibid.*, 1935, [*A*], **150**, 220; M. Ritchie, *Nature*, 1935, **136**, 221.

[59] A. O. Allen and O. K. Rice, *J. Amer. Chem. Soc.*, 1935, **57**, 310.

[60] E. E. Aynsley, T. G. Pearson, and P. L. Robinson, *J.*, 1935, 58.

[61] C. N. Hinshelwood, A. T. Williamson, and J. H. Wolfenden, *Proc. Roy. Soc.*, 1934, [*A*], **147**, 48.

The number of recorded chemical phenomena which find their readiest interpretation in terms of the chain theory is rapidly increasing.[67b] For example, R. G. W. Norrish[68] has shown that the oxidation of hydrocarbons—now definitely established as a direct attack by oxygen[69]—which yields such complicated analytical and kinetic results, can be represented in terms of quite a simple chain mechanism. A helpful summarising article on this subject has also been given by W. Jost.[70] Polymerisation reactions offer special opportunities for displaying the power of the chain theory.[71] These interesting chemical changes are gaining a new importance; but the time does not seem ripe for discussing them in these Reports. We shall, however, refer to them again in a later section. The chain theory itself has been elaborated in two directions. To account for the widening out of the explosion limits consequent upon the introduction of artificially generated chain centres, N. Semenoff[72] has postulated a mutual interference of the chains. In order to explain the rapidity with which explosion waves travel in detonations, K. K. Andréew and J. B. Chariton[73] invoke the idea of macro-chains. New experiments to which the less elaborate theory has been applied include those on the explosion of ethyl azide,[74] the oxidation of propaldehyde,[75] the chlorination of propane,[76] the polymerisation of formaldehyde,[77] the reaction between carbon monoxide and nitrous oxide,[78] and the effect of hydrogen on the carbon monoxide flame.[79]

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[62] M. Prettre, *Compt. rend.*, 1935, **200**, 132.

[63] G. Gorchakov and L. Lavrov, *Acta Physicochimica U.R.S.S.*, 1934, **1**, 139.

[64] H. G. Tanner, *J. Amer. Chem. Soc.*, 1934, **56**, 2250.

[65] D. L. Chapman and G. Gregory, *Proc. Roy. Soc.*, 1934, [*A*], **147**, 68.

[66] W. E. Garner and H. J. Willavoys, *Trans. Faraday Soc.*, 1935, **31**, 805.

[67] *Ibid.*, p. 452. [67a] *Z. physikal. Chem.*, 1935, [*B*], **30**, 265.

[67b] N. Semenoff, "Chemical Kinetics and Chain Reactions," Oxford, 1935.

[68] *Proc. Roy. Soc.*, 1935, [*A*], **150**, 36.

[69] W. A. Bone and J. Bell, *ibid.*, 1934, [*A*], **144**, 257.

[70] *Z. Elektrochem.*, 1935, **41**, 186.

[71] H. Dostal and H. Mark, *Z. physikal. Chem.*, 1935, [*B*], **29**, 299; G. Gee and E. K. Rideal, *Trans. Faraday Soc.*, 1935, **31**, 969. A Report of the Faraday Society's Discussion on Polymerisation is to be published in 1936. A preliminary survey (E. K. Rideal, *Nature*, 1935, **135**, 626) has already appeared.

[72] *Z. physikal. Chem.*, 1935, [*B*], **28**, 31.

[73] *Trans. Faraday Soc.*, 1935, **31**, 797.

Brief mention must be made of the increasing variety of decomposition reactions which have been recently studied. The following compounds decompose by a unimolecular mechanism in the homogeneous gas phase: methyl [80] and *sec.*-butyl [81] iodides; nitromethane; [82] methyl,[83] *n*-propyl,[84] and *iso*propyl [85] nitrites; and glyoxal.[86] Only the primary step in the decomposition of methylamine [87] is homogeneous; increased surface inhibits the rate of decomposition of propylamine,[88] an effect which is apparently absent in the case of triethylamine.[89] An interesting example of intermolecular conversion obeying the unimolecular law is the isomerism of *cis*-methyl cinnamate.[90] Bimolecular behaviour is exhibited by the polymerisation and hydrogenation of acetylene,[91] by the decomposition of nitrosyl chloride,[92] and predominantly by the decomposition of acraldehyde.[93] The effect of iodine on the rate of decomposition of chloral [94] is consistent with a bimolecular mechanism involving iodine atoms; catalysis by nitric oxide is similarly interpreted.[95] The decomposition of nickel carbonyl [96] follows a more complicated course.

[74] H. C. Campbell and O. K. Rice, *J. Amer. Chem. Soc.*, 1935, **57**, 1044.

[75] E. W. R. Steacie, W. H. Hatcher, and S. Rosenberg, *J. Physical Chem.*, 1934, **38**, 1189.

[76] S. Yuster and L. H. Reyerson, *ibid.*, 1935, **39**, 859.

[77] J. E. Carrothers and R. G. W. Norrish, *Nature*, 1935, **135**, 582.

[78] C. E. H. Bawn, *Trans. Faraday Soc.*, 1935, **31**, 461.

[79] W. E. Garner and F. H. Pollard, *J.*, 1935, 144.

[80] E. W. R. Steacie and R. D. Macdonald, *J. Amer. Chem. Soc.*, 1935, **57**, 488.

[81] R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 482.

[82] H. A. Taylor and V. V. Vesselovsky, *J. Physical Chem.*, 1935, **39**, 1095.

[83] E. W. R. Steacie and G. T. Shaw, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 388.

[84] *Idem*, *J. Chem. Physics*, 1935, **3**, 345.

[85] *Idem*, *Proc. Roy. Soc.*, 1935, [*A*], **151**, 685.

[86] E. W. R. Steacie, W. H. Hatcher, and J. F. Harwood, *J. Chem. Physics*, 1935, **3**, 291.

[87] H. J. Emeléus and L. J. Jolley, *J.*, 1935, 929.

[88] D. V. Sickman and O. K. Rice, *J. Amer. Chem. Soc.*, 1935, **57**, 22.

[89] H. A. Taylor and E. E. Juterbock, *J. Physical Chem.*, 1935, **39**, 1103.

[90] G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, 1935, **57**, 269.

[91] H. A. Taylor and A. van Hook, *J. Physical Chem.*, 1935, **39**, 811.

[92] G. Waddington and R. C. Tolman, *J. Amer. Chem. Soc.*, 1935, **57**, 698.

[93] H. W. Thompson and J. J. Frewing, *J.*, 1935, 1443.

[94] F. H. Verhoek and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 334.

[95] F. H. Verhoek, *Trans. Faraday Soc.*, 1935, **31**, 1521.

[96] A. P. Garratt and H. W. Thompson, *J.*, 1934, 1822; C. E. H. Bawn, *Trans. Faraday Soc.*, 1935, **31**, 461.

Reactions in Solution.—Advances in this field have depended more on the correct interpretation of existing data than on the discovery of new reactions. Our virtual ignorance of the nature of interaction in the condensed phase, long used as an excuse for shunning the problem, is now recognised as a reason for studying it.

Many of the reactions which proved helpful in instituting a co-ordinated theory of reactions in solution have been reinvestigated, with confirmatory results. To the sole instance previously known, two others have been added ($C_2H_4I_2 + I \longrightarrow C_2H_4 + I_2 + I$ and $O_2 + p\text{-}H_2 \longrightarrow O_2 + o\text{-}H_2$) of bimolecular reactions which have been measured in the gas phase and in solution : [97, 98] they have the same E and k in the two phases. These results afford the most direct knowledge we have of the frequency of binary collisions in dilute solution. They support the anticipations of Christiansen (1923), Tolman (1927), and others that Z is of the same order of magnitude in the two systems. A third example ($COS + H_2O \longrightarrow CO_2 + H_2S$) gives $E = 25{,}700$ for the predominantly homogeneous gas reaction, and $E = 22{,}700$ for the condensed reaction; collisions in the latter case, however, are between solute and solvent molecules; if their frequency is calculated by the equation ${}_1Z_s = 3\pi\eta\sigma/2m$, E for the condensed reaction becomes 26,300 cals.[99] Further analogies between collision frequencies in the two systems may be drawn from the work on quenching of fluorescence in gases and liquids.[1] A. W. Chapman [2] has shown that the velocity of the Beckmann transformation of benzophenoneoxime picryl ether, catalysed by a variety of substances in carbon tetrachloride, has the same value as that computed for the hypothetical gas reaction, the observed E's and the gas kinetic collision formula being used. The assumption that reactions of the type $R_1ONa + R_2Cl \longrightarrow R_1OR_2 + NaCl$ are chiefly ionic, involving R_1O' ions, has been justified by more reliable determinations of the degree of dissociation.[3] The similarity of the k's for homologous reactions has been discussed in terms of the theory of coupled oscillators.[4] The distinction drawn between these etherifications and reactions of the type $R_1R_2R_3N + R_4Cl \longrightarrow R_1R_2R_3R_4NCl$ has been heightened by the response of the two to high pressures, which has been accur-

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[97] *Loc. cit.*, ref. (9), p. 93.

[98] L. Farkas and H. Sachsse, *Z. physikal. Chem.*, 1933, [*B*], **23**, 1.

[99] H. W. Thompson, C. F. Kearton, and S. A. Lamb, *J.*, 1935, 1033.

[1] J. Franck and H. Levi, *Z. physikal. Chem.*, 1934, [*B*], **27**, 409.

[2] *J.*, 1934, 1550; 1935, 1223; see also K. D. Anderson and D. Ll. Hammick, *ibid.*, p. 30.

[3] P. J. Hardwick, *ibid.*, 1935, 141.

[4] H. Pelzer, *Z. Elektrochem.*, 1934, **39**, 608.

ately studied.[5] The rate of formation of urea and of monomethylurea to form cyanate ions and the corresponding cations has been the subject of precise and extensive work in various media,[6] enabling the relation between critical increment and ionic strength to be verified and elaborated.[7] The expected independence of E of electrolyte concentration has been demonstrated for numerous reactions of zero ionic type, including the acid hydrolysis of diethylacetal [8] and ethyl acetate,[9] and the basic hydrolysis of the acetylglycollate ion, for which over 300 values of E have been published.[10] The value of E recently found for the mutarotation of glucose in water (18,000) [11] is in better agreement with the classical value of 17,700 given by Hudson and Dale in 1917 than with the amended value of 19,300 published by Kilpatrick in 1931. The rates of reactions of the type $R_1R_2S + R_3Cl \longrightarrow R_1R_2R_3SCl$ have hitherto been inferred quantities; direct measurements have now been made in various solvents.[12] Distinctly less attention is being paid to the study of reactions of the first and the third order. New instances of the unimolecular cleavage of carbon dioxide from acids have, however, been examined,[13] and the alleged termolecular reaction between stannous and ferric chlorides has been shown to be fairly complicated.[14] The latter change bears many of the distinguishing features of a chain reaction, though it has not yet been discussed from this angle. The search is also being continued for a satisfactory explanation of the kinetics of those complicated reactions involving halide, hypohalite, halite, and halate ions in aqueous solution.[15]

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[5] E. W. Fawcett and R. O. Gibson, *J.*, 1934, 386; R. O. Gibson, E. W. Fawcett, and M. W. Perrin, *Proc. Roy. Soc.*, 1935, [*A*], **150**, 223.

[6] (Miss) C. C. Miller, *ibid.*, 1934, [*A*], **145**, 288; 1935, [*A*], **151**, 188.

[7] J. C. Warner and collaborators: with F. B. Stitt, *J. Amer. Chem. Soc.*, 1933, **55**, 4807; with E. L. Warrick, *ibid.*, 1935, **57**, 1491; with W. J. Svirbely, *ibid.*, p. 1883.

[8] L. C. Riesch and M. Kilpatrick, *J. Physical Chem.*, 1935, **39**, 561.

[9] W. Wylzałkowska, *Rocz. Chem.*, 1934, **14**, 1118.

[10] A. von Kiss and R. Kukai, *Z. anorg. Chem.*, 1935, **223**, 149; *Rec. trav. chim.*, 1935, **54**, 337.

[11] E. A. Moelwyn-Hughes, R. Klar, and K. F. Bonhoeffer, *Z. physikal. Chem.*, 1934, **169**, 113.

[12] J. K. Syrkin and I. T. Gladischew, *Acta Physicochimica U.R.S.S.*, 1935, **2**, 291.

[13] (Miss) J. Muus, *J. Physical Chem.*, 1935, **39**, 343; K. Beniya, *J. Biochem. Japan*, 1934, **20**, 451.

[14] R. A. Robinson and N. H. Law, *Trans. Faraday Soc.*, 1935, **31**, 899.

[15] H. A. Liebhafsky, *J. Amer. Chem. Soc.*, 1934, **56**, 2369; R. M. Chapin, *ibid.*, p. 2212; W. C. Bray and H. A. Liebhafsky, *ibid.*, p. 51; R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, 1935, **31**, 868; A. Skrabal and H. Schreiner, *Monatsh.*, 1935, **65**, 213; C. F. Prutton and S. H. Maron, *J. Amer. Chem. Soc.*, 1935, **57**, 1652.

Four of the directions in which the subject is advancing may be indicated roughly by the terms rapid reactions, radical reactions, exchange reactions, and film reactions.

The application of Hartridge and Roughton's technique [16] offers a means of extending the range of observable phenomena in solution. In the hands of H. von Halban and H. Eisner,[17] preliminary conclusions are already derived concerning numerous organic and inorganic reactions which are half completed in about 0·001 second, and further useful information may confidently be expected from this source. The methods of measuring the speed of reactions in solution have formed the subject of a recent biochemical discussion.[18]

The part played by free radicals in solution becomes more prominent. E. Abel and K. Hilferding [19] accept the mechanism proposed by Griffith and McKeown (1932) for the action of aqueous iodine on oxalic acid. One of the three rate-determining steps is $I + C_2O_4'' \longrightarrow C_2O_4' + I'$, with $E = 19{,}000$, and a chain length of a few million cycles. The function of HO_2 in the decomposition of aqueous hydrogen peroxide has been quantitatively studied.[20] J. R. Velasco [21] finds that the relative rates of reaction of ketones with diphenylsemicarbazide are exponentially related to their oxidation potentials; and a complementary relation apparently holds for the inhibitive action of foreign substances on the reduction of mercuric chloride by picric acid.[22] The energetics of some of the steps in radical chains thus become amenable to measurement.

Experiments on the replacement of the hydrated proton by the hydrated deuteron showed that the ratio $\alpha = k_{D_2O^{\cdot}}/k_{H_2O^{\cdot}}$ is less than 1 for the mutarotation of glucose, and that $d\alpha/dT$ is positive; [23] for the inversion of cane sugar, α exceeds 1, and $d\alpha/dT$ is negative.[24] The hydrolysis of methyl acetate [25] runs parallel to the case of sucrose. By applying the theory of multiple catalysis, the value of k_{HOD} has since been estimated at 25°.[26] E for the pseudo-unimolecular reaction $CH_3{\cdot}CO{\cdot}CH_3 + HOD \longrightarrow CH_3{\cdot}CO{\cdot}CH_2D + HOH$ is 18,000 cals.;[27] α appears to be very nearly unity for hydrolytic reactions catalysed by enzymes[28]—a result which allows us to eliminate one of the many explanations possible for the arresting effect of heavy water on the growth of organisms.[29]

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[16] See R. Brinkman, R. Magaria, and F. J. W. Roughton, *Phil. Trans.*, 1933, [*A*], **232**, 65.

[17] *Helv. Chim. Acta*, 1935, **18**, 724.

[18] A. V. Hill, H. Freundlich, H. Hartridge, G. Millikan, F. J. W. Roughton, E. K. Rideal, J. B. S. Haldane, M. Polanyi, and McK. Cattell, *Proc. Roy. Soc.*, 1934, [*B*], **116**, 185.

[19] *Z. physikal. Chem.*, 1935, **172**, 353.

[20] G. Kornfeld, *ibid.*, 1935, [*B*], **29**, 205; J. Weiss, *Trans. Faraday Soc.*, 1935, **31**, 668; *Naturwiss.*, 1935, **23**, 64.

[21] *Anal. Fis. Quim.*, 1935, **32**, 345; cf. B. F. Chow, *J. Amer. Chem. Soc.*, 1935, **57**, 1437.

[22] K. Weber, *Z. physikal. Chem.*, 1935, **172**, 459.

[23] E. A. Moelwyn-Hughes, *ibid.*, 1934, [*B*], **26**, 272.

[24] E. A. Moelwyn-Hughes and K. F. Bonhoeffer, *Naturwiss.*, 1934, **22**, 174.

[25] J. C. Hornel, *Nature*, 1935, **135**, 909.

[26] W. H. Hammill and V. K. LaMer, *J. Chem. Physics*, 1934, **2**, 891.

The relatively simple technique required to measure the surface potential of films[30] is a new and powerful implement in the hands of the investigator, enabling him, as it were, almost to touch the molecules which are reacting. With investigations of the hydrolysis of proteins,[31] the oxidation of fatty acids,[32] the saponification of esters,[33] and the polymerisation of unsaturated compounds,[34] the subject of chemical kinetics in two dimensions may be said to have begun.[35]

Remarks on the Semi-empirical Factor, P.—The velocity constant for bimolecular reactions may be written in the form $k = PZe^{-E/RT}$, where Z is the collision frequency. In the case of simple reactions, P gives the probability that an energetically satisfying encounter leads to chemical change. The meaning of P, often called the " steric " factor, is in other cases more obscure, and must be discussed briefly. We shall accept the value of Z given by the kinetic theory of gases, although the use of formulæ differing from it both in form[36, 37] and in order of magnitude[38, 16] has been advocated. P is known to be unity for some hundreds of reactions in solution and for some tens of reactions in gases. It may also be as high as 10^{+9} or as low as 10^{-9}. Reactions are said to have normal, fast, or slow rates, according as P equals, exceeds, or is less than 1. When two comparable reactions have different rates, experiment shows that the difference may be due to a change in E, in P, or in both. For example, when hydrogen chloride is replaced by hydrogen bromide in the chloroacetanilide reaction,[39] the 20,000-fold increase in speed is due almost entirely to a change in E. When an ionic reaction is compared with the corresponding non-ionic one, it often happens that E remains constant while $P_{\pm}$ is about 1 and P_0 is lower by several powers of ten. Concurrent changes in P and E are very common.

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[27] L. J. Halford, L. C. Anderson, J. R. Bates, and R. D. Swisher, *J. Amer. Chem. Soc.*, 1935, **57**, 1663.

[28] E. W. R. Steacie, *Z. physikal. Chem.*, 1934, [*B*], **27**, 6; **28**, 236.

[29] O. Reitz and K. F. Bonhoeffer, *ibid.*, 1934, **172**, 369; 1935, **174**, 424.

[30] A. H. Hughes, J. H. Schulman, and E. K. Rideal, *Nature*, 1932, **129**, 21.

[31] J. H. Schulman and E. K. Rideal, *Biochem. J.*, 1933, **27**, 1581.

[32] A. H. Hughes and E. K. Rideal, *Proc. Roy. Soc.*, 1933, [*A*], **140**, 253.

[33] R. J. Fosbinder and E. K. Rideal, *ibid.*, 1933, [*A*], **143**, 61.

[34] See Ref. 71.

[35] Cf. E. J. Bowen, *Ann. Reports*, 1934.

[36] J. K. Syrkin, *Acta Physicochimica U.R.S.S.*, 1935, **1**, 855.

[37] R. S. Bradley, *J.*, 1934, 1910.

[38] M. G. Evans and M. Polanyi, *loc. cit.*, ref. (15), p. 94.

[39] I. Jones and F. G. Soper, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 643.

There has been no lack of ideas in attempting to interpret P. Some of the earlier conjectures were disproved by the experiments of Hinshelwood and Moelwyn-Hughes (1932), who pointed out new possible meanings which may be attached to it. There are three aspects of recent discussions.

(1) The geometric factor, which aims at allowing for orientation effects. Opinions on the possible extent of this contribution vary largely. It should, perhaps, be pointed out that the effect is to some extent automatically allowed for in the dynamical formulation of the problem.[40] J. M. Sturtevant,[41] on theoretical grounds, concludes that the orientation effect is not large enough to allow for the relatively minor deviations from the laws of Brönsted and LaMer.[42] With different experimental systems, on the other hand, A. T. Williamson and C. N. Hinshelwood [43] consider that a factor of the order of 10^{-3} " could reasonably be explained on the basis of the simplest kind of steric considerations "—a view which is endorsed by R. P. Bell and (Sir) R. V. H. Levinge.[44]

(2) The transmission probability, G, which, according to H. Hellmann and J. K. Syrkin,[45] can be considerably smaller than 1, even for massive particles, provided G is computed for each discrete state. Thus the ease with which the nitrogen atom in ammonia can pass to and fro through the plane of the three hydrogen atoms appears to be sensitive to the degree of sharpness of the quantisation of vibrational energy.

(3) The entropy change, S. Drawing on thermodynamical analogy, we may anticipate that E varies linearly with the temperature ($E = E_0 + ST$), in which case P includes a term $e^{S/R}$. In principle, S can be found from the temperature variation of E or from the postulated structure of the critical complex (Soper,[22] LaMer,[22] Rodebush,[15] Wynne-Jones and Eyring [21]). Provided we know the actual equilibrium data for reactants $\rightleftharpoons$ resultants, as distinct from the hypothetical equilibrium data for reactants $\rightleftharpoons$ reactive complex, we can eliminate the unknown term involving the entropy of activation, and obtain expressions for the velocity

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[40] R. C. Tolman, " Statistical Mechanics," p. 67, 1927.

[41] *J. Chem. Physics*, 1935, **3**, 295.

[42] A full account of these laws, and of salt effects in general, was given by R. P. Bell in the *Annual Reports* for 1934. Subsequent developments have been hardly sufficient to warrant discussion here.

[43] *Trans. Faraday Soc.*, 1934, **30**, 1145; A. C. Rolfe and C. N. Hinshelwood, *ibid.*, p. 935.

[44] *Proc. Roy. Soc.*, 1935, [*A*], **151**, 211.

[45] *Acta Physicochimica U.R.S.S.*, 1935, **3**, 433.

of reaction which include only measurable entropy terms. A fair test of the theory in this least speculative form has been carried out by F. G. Soper[46] for bimolecular reactions in the gaseous phase and in solution. There is satisfactory agreement for cases with P differing as widely as 1 and 10^{-7}. According to Soper, P always approximates to unity for reactions attended by an increase in entropy. The theory, therefore, applies in particular to slow reactions, the outstanding examples of which were shown, some years ago, to be highly exothermic.

A method of factorising the more complicated term P for unimolecular reactions has been suggested by C. N. Hinshelwood.[34] In addition to the geometric contribution, and a correction term superimposed on the Boltzmann factor, a third term α/β is introduced, where α is the rate at which energy in the preactivated molecule flows into the requisite bond, and β is the rate at which it flows elsewhere, *i.e.*, is dissipated. The internal redistribution of energy has also been the topic of an organised discussion.[47]

Organic Reactions.—We must regrettably confine ourselves to a mere categorical list of selected organic reactions which have been studied with sufficient care to allow the detection of even small changes in P or in E. Apart from the unimolecular decomposition of nitrites, and the *cis–trans*-isomerism of stilbene, methyl cinnamate, and methyl maleate,[48] the study of reactions in families has been confined to bimolecular reactions in solution. In the following examples, each consists of about twelve members: reactions of aryl and alkyl chlorides with ethyl alcohol in various solvents;[49] saponification of esters of different substituted phthalic[50] and crotonic acids;[51] reactions between hydrogen bromide and alcohols in phenol solution;[52] reactions between bases and $p\text{-}C_6H_4R\cdot CH_2Br$ in various solvents;[53] organic esterifications;[54] the union of amines with halides in benzene solution;[55] the hydrogen-ion catalysed prototropy of nuclear substituted acetophenones,[56] which affords an additional illustration of Nathan and Watson's rule (1933); and the action of alkali on bromoethanes and chloroethanes.[57] The theory of the constitutional effects upon the kinetics of organic reactions has been developed considerably in the light of new work.[58] The distinction between organic and physical chemistry, perhaps seldom more than a convention, seems to vanish completely when we find that mesomerism, for example, may be directly interpreted as a resonance effect between molecules possessing normal and polar structure.[59]

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[46] *J.*, 1935, 1393.

[47] C. N. Hinshelwood, J. E. Lennard-Jones, M. Travers, M. Polanyi, C. Zener, E. J. Bowen, R. G. W. Norrish, H. W. Thompson, C. J. M. Fletcher, E. K. Rideal, and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 239.

[48] G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, 1935, **57**, 269.

[49] J. F. Norris, E. V. Vasce, and J. C. J. Staud, *ibid.*, p. 1415; J. F. Norris and H. H. Young, *ibid.*, p. 1420; J. F. Norris and E. C. Haines, *ibid.*, p. 1425.

[50] G. Semerano, *Gazzetta*, 1935, **65**, 252.

[51] E. Schjanberg, *Z. physikal. Chem.*, 1935, **174**, 465.

[52] G. M. Bennett and F. M. Reynolds, *J.*, 1935, 131.

[53] J. W. Baker and W. S. Nathan, *ibid.*, p. 519.

[54] C. N. Hinshelwood and A. R. Legard, *ibid.*, pp. 587, 1588.

[55] C. A. Winkler and C. N. Hinshelwood, *ibid.*, p. 1147.

E. A. M.-H.

6. SURFACE CHEMISTRY.

A considerable and increasing amount of work has been done in this field during the period under review. It is difficult to select sections for special comment; but outstanding interest is perhaps attached to the nature of adsorption processes of chemical or so-called " activated " type and to the degree to which those of slower form are due to penetration effects; also to the recognition and measurement of the energy barriers which are involved in the activated migration theory which has recently been put forward by E. K. Rideal. Further, in heterogeneous catalysis, the attempted analysis by H. zur Strassen and G. M. Schwab of the factors which are contributory to the apparent energies of activation appears undoubtedly an important step towards the attachment of some degree of precise significance to the experimental values of those energy terms which are obtained on the basis of the temperature coefficient.

Adsorption Components.—In certain cases of adsorption, the process is obviously composite and consists—in addition to low-temperature adsorption of van der Waals type—of a relatively rapid component, which in all probability involves linkage of a purely chemical nature, and of a slower process which takes place concurrently with or subsequently to the primary process. This sharply differentiated, very rapid component is especially characteristic of the adsorption of hydrogen and of certain other gases by metals, such as platinum or nickel, which are active for catalytic hydrogenation. In other cases, *e.g.*, in the adsorption of many gases on adsorbents of oxide type, this distinct rapid component is less pronounced or absent.

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[56] D. P. Evans, V. G. Morgan, and H. B. Watson, *J.*, 1935, 1167, 1174.

[57] W. Taylor, *ibid.*, p. 1514; W. Taylor and A. M. Ward, *J.*, 1934, 2003.

[58] J. L. Gleave, E. D. Hughes, and C. K. Ingold, *J.*, 1935, 236; E. D. Hughes and C. K. Ingold, *ibid.*, p. 244; E. D. Hughes, *ibid.*, p. 255; C. K. Ingold and H. G. G. Mohrhenn, *ibid.*, p. 1482; L. P. Hammett, *Chem. Reviews*, 1935, **17**, 125.

[59] C. K. Ingold, *ibid.*, 1934, **15**, 225; H. B. Watson, W. S. Nathan, and L. L. Laurie, *J. Chem. Physics*, 1935, **3**, 170.

In the last Report in which a review of the progress of surface chemistry was included (1931), an account was given of H. S. Taylor's conception of activated adsorption. This has in the meantime been developed in a number of papers; and the treatment of the subject has become less simple by the apparent presence, in many cases, of more than one activated component. Thus H. S. Taylor and C. O. Strother,[1] who continued the work of H. S. Taylor and D. V. Sickman,[2] have put forward, in connexion with the adsorption of hydrogen on zinc oxide, evidence for two activated adsorption processes, in addition to van der Waals adsorption. The first of these activated processes takes place between 0° and about 100°, and is associated with an activation energy of the order of 5 kg.-cals. The second, which begins at about 100° and is still measurable at about 300°, has an activation energy of about 12 kg.-cals. Physical adsorption took place up to about − 80°; and there was no measurable adsorption of this type at or above room temperature. With zinc oxide promoted with chromium oxide, which is a more active catalyst, the existence of only one form of activated adsorption, beginning at − 78°, was deduced; and this low initial temperature is regarded as being indicative of an extremely low activation energy. The calculated values of these activation energies vary with the conditions: for instance, J. Howard and H. S. Taylor[3] found that the apparent energy of activation of the activated adsorption of hydrogen on chromium oxide varied, with the sample of oxide studied, from 14 kg.-cals. to about twice this value and increased with the degree of covering. A similar apparent increase in the critical increment with the adsorbed concentration has been observed by P. V. McKinney[4] for hydrogen on manganese chromite.

If the adsorption of hydrogen or of another reducing gas on an oxide is involved, the possibility of the reduction of the oxide is always present. There appear, however, to be good grounds for assuming in many such cases the prior formation of an adsorption complex, which breaks down, on being further heated, into the normal reduction products; and the total reaction may thus be regarded as including an initial process of irreversible adsorption. McKinney has investigated from this standpoint the adsorption of carbon monoxide by palladium oxide,[5] which is only slowly reduced by this gas even at 100°. At − 80° the adsorption was almost entirely of the physical type; but irreversible activated adsorption began at about 0° and increased with increasing temperature to a maximum at about 110°, beyond which temperature adsorption decreased. The isobar thus showed all the normal characteristics of activated adsorption. Evaporation of the adsorbed gas only took place in the form of carbon dioxide. McKinney calculated the apparent energy of activation of the adsorption process, but regards the wide variation in the values obtained (2·6—16 kg.-cals.) as an indication of the complex nature of the adsorption. The formation of irreversible adsorption complexes has also, for instance, been postulated by W. E. Garner and F. J. Veal [6] in the adsorption of carbon monoxide on a zinc chromite catalyst; and a slightly different type of irreversible activated adsorption is represented by the work of W. W. Russell and L. G. Ghering on the adsorption of oxygen by nickel at low temperatures.[7]

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[1] *J. Amer. Chem. Soc.*, 1934, **56**, 586; *A.*, 1934, 484.

[2] *Ibid.*, 1932, **54**, 602; *A.*, 1934, 458.

[3] *Ibid.*, 1934, **56**, 2259; *A.*, 1935, 28.

[4] *J. Physical Chem.*, 1933, **37**, 381; *A.*, 1933, 471.

Since the subject is not complicated by the possibility of reduction, the investigation of activated adsorption on metals is of special interest. R. W. Harkness and P. H. Emmett [8] have adduced evidence for two types of activated adsorption, in addition to physical adsorption, for hydrogen on promoted ammonia catalysts; and J. Turkevich and H. S. Taylor [9] have examined, from the standpoint of an activated component, the adsorption of ethylene on hydrogenating catalysts both of metallic and of oxide type. With manganese chromite, the adsorption of ethylene at or below 0° is principally of the van der Waals form. At 110° there was, in addition, some activated adsorption. With copper, activated adsorption occurs at a much lower temperature, *viz.*, even at 0°. The isotherms for both types of catalyst were of the form in which the adsorption rises continuously with increasing pressure. A further example of a somewhat similar nature to the already cited adsorption of oxygen by nickel is its adsorption by platinum. H. Reischauer [10] obtained, with compact platinum, indications of two types of activated adsorption, which are associated with different activation energies and occur at different ranges of temperature.

The conception of activated adsorption, in which the interaction between the gas and the adsorbent is regarded as being composed of activated surface processes, has been criticised by many investigators. For instance, Garner and Veal [11] consider that there is but little evidence that this type of adsorption is controlled by activation energy inherent in the adsorption process itself. Certainly, the degree of significance of the widely varying values which are obtained, on the basis of the temperature coefficient, for the apparent activation energy needs further definition; and much is to be said for Garner and Veal's preference for the older designation, chemisorption, to indicate the nature of the linkage and to distinguish such processes from physical adsorption, rather than the application of the term " activated " to processes for which the rate-control by activation energy of adsorption is still a matter on which agreement has not been reached.

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[5] *J. Amer. Chem. Soc.*, 1933, **55**, 3626; *A.*, 1933, 913. [6] *J.*, 1935, **1487.**

[7] *J. Amer. Chem. Soc.*, 1933, **55**, 4468; *A.*, 1934, 22.

[8] *Ibid.*, p. 3496; *A.*, 1933, 1018; 1934, **56**, 490; *A.*, 1934, 371.

[9] *Ibid.*, 1934, **56**, 2254; *A.*, 1934, 28.

[10] *Z. physikal. Chem.*, 1934, [*B*], **26**, 399; *A.*, 1934, 1303.

In this connexion, the degree of influence of any penetration effects in the total slow adsorption process is still to be considered. This aspect was discussed by E. W. R. Steacie,[12] A. F. H. Ward,[13] and J. E. Lennard-Jones,[14] as already reported,[15] and also by S. Iijima,[16] who concurs in the view that the rate curves obtained for hydrogen on, *e.g.*, finely divided nickel indicate adsorption followed by diffusion. The subject of penetration has more recently been developed by E. K. Rideal [17] in collaboration with H. W. Melville.[18] The total adsorption is regarded as consisting of at least three processes involving energy barriers, *viz.*, the passage from van der Waals adsorption to chemisorption, migration from just outside to just inside the surface, and internal migration. Evidence was adduced, in the course of work with hydrogen and with deuterium, for the existence of a definite energy barrier for the penetration of these gases from the surface to the interior of copper, as well as for migration within the metal. Accordingly, the slow adsorption process, which proceeds with an apparent energy of activation, is apparently a composite reaction; and any data, *e.g.*, for the activation energy, only acquire significance if the degree of incidence of each component can be determined. The surface factor in these composite processes may be recognised from many observations. J. Howard [19] found that the high-temperature chemisorption of hydrogen on chromium oxide gel markedly diminishes the van der Waals adsorption, from which he concludes that the slow high-temperature process is at least in part a surface phenomenon. P. H. Emmett and R. W. Harkness[20] reach the same conclusion from the effect of previous high-temperature adsorption on the rate of the ortho-para conversion of hydrogen on platinum or nickel at − 190° and from a study of adsorption on iron–ammonia catalysts.[21]

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[11] *Loc. cit.*, ref. (6).

[12] *J. Physical Chem.*, 1931, **35**, 2112; *A.*, 1931, 904.

[13] *Proc. Roy. Soc.*, 1931, [*A*], **133**, 506, 522; *A.*, 1931, 1365; *Trans. Faraday Soc.*, 1932, **28**, 399; *A.*, 1932, 688.

[14] *Ibid.*, p. 333; *A.*, 1932, 688.

[15] *Ann. Reports*, 1931, **28**, 37, 38.

[16] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1933, **22**, 285; **23**, 34; *A.*, 1934, 139, 358.

[17] *Nature*, 1935, **135**, 737; *A.*, 818.

[18] *Proc. Roy. Soc.*, 1935, [*A*], **153**, 77, 89.

[19] *Nature*, 1933, **132**, 603; *A.*, 1933, 1112.

Heat of Adsorption.—In calorimetrically determined adsorption heats, the effect measured will, in cases such as the adsorption of hydrogen by metals, represent principally that due to the rapid component; and, in view of the difficulty in previously removing the last traces of adsorbed gases without exposure of the adsorbent to a temperature sufficient to modify its normal surface properties, the initially observed differential heat will not, in general, be the true threshold value. This is especially the case for hydrogenating catalysts such as platinum or nickel. If, on the other hand, the adsorption heat is calculated by means of the Clausius–Clapeyron equation, the significance of the result will depend on the attainment of true equilibrium and on the effective simplicity of the adsorption studied.

In exceptional cases, however, threshold values for the adsorption heat may be measured. J. K. Roberts,[22] who used the value of the thermal accommodation coefficient of neon as an indication of the degree of bareness of a tungsten filament, previously flashed at a temperature above 2000°, has calculated a threshold heat of about 45 kg.-cals. per mol. of hydrogen for the adsorption of this gas on tungsten. The adsorption heat subsequently decreases to a limit of about 18 kg.-cals. for a completely covered tungsten surface, the decrease being regarded as due to the nature of the adsorption process and not necessarily to any heterogeneous character of the surface. The adsorption was practically instantaneous, even at pressures of 10^{-4} mm. or less.

Under the conditions which obtain when the adsorption heat is measured for a previously degassed catalytically active metal, the surface is already, in general, partially covered; and the apparently constant values for the differential adsorption heat which have been obtained by various investigators[23] for hydrogen on copper or platinum, or for oxygen on platinum, may be due to the restricted adsorption range imposed by the limitations of degassing, or to a difference in the adsorptive properties of finely divided metallic catalysts and a previously heated compact metal filament. For carbon monoxide on reduced copper, R. A. Beebe and E. L. Wildner [24] observed an adsorption heat which decreased with the adsorbed concentration. It may be noted that, in a composite adsorption, an increased degree of incidence of slower and less exothermic components as the adsorbed concentration is increased, would, under the conditions of calorimetric measurements, in itself cause a fall in the observed heat as the degree of covering is increased.

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[20] *J. Amer. Chem. Soc.*, 1935, **57**, 1624; *A.*, 1329.

[21] *Ibid.*, p. 1631; *A.*, 1315.

[22] *Proc. Roy. Soc.*, 1935, [*A*], **152**, 445.

[23] A. F. H. Ward, *loc. cit.*; R. A. Beebe, *Trans. Faraday Soc.*, 1932, **28**, 761; *A.*, 1932, 1199; E. B. Maxted and N. J. Hassid, *J.*, 1931, 3313; *A.*, 1932, 118; *Trans. Faraday Soc.*, 1933, **29**, 688; *A.*, 1933, 911.

In any case, the direct determination of adsorption heats presents considerable experimental difficulty. Possible sources of error have been discussed by Ward and by others of the above workers, also by G. M. Schwab and W. Brennecke.[25] Note may also be made of a particularly accurate form of calorimeter which has recently been described by W. E. Garner and F. J. Veal.[26] The direct measurement of the adsorption heat of hydrogen and of carbon monoxide on zinc oxide and on zinc chromite in this apparatus gave evidence of two types of adsorption for the latter adsorbent, which was also employed in the partially reduced state, namely, an irreversible adsorption, associated with a heat of about 45 kg.-cals., which takes place on the oxidised surface, and, on the reduced surface, a reversible adsorption having a heat effect of 10—15 kg.-cals.

As an example of a system containing a metallic adsorbent and in which the conditions permit the thermodynamic calculation of the adsorption heat, the adsorption of oxygen on silver may be mentioned. A. F. Benton and L. C. Drake [27] have calculated in this way a value of about 13 kg.-cals. for the adsorption at about 190°, at a pressure such that the formation of silver oxide is precluded. Frequently, however, with metals, this indirect method of calculation is inapplicable owing either to non-attainment of equilibrium or to lack of knowledge with regard to the effective simplicity of the adsorption.

Calculation by means of the Clausius–Clapeyron equation can, however, be applied to many adsorbents of oxide type. H. S. Taylor and D. V. Sickman [28] obtained by this method a value of 1·1 kg.-cals. for the physical adsorption of hydrogen on zinc oxide at low temperatures, and about 21 kg.-cals. for the adsorption process which takes place at about 450°. Further, as an instance of a relatively high-temperature adsorption accompanied by a far smaller heat effect, B. Neumann and E. Goebel [29] have attempted to estimate the influence of temperature on the heat of adsorption of oxygen on iron oxide. Great accuracy was not possible, but the adsorption heat apparently fell from 2·2 kg.-cals. for a temperature range of 20—100° to 1·3 kg.-cals. when the upper temperature was increased to 300°.

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[24] *J. Amer. Chem. Soc.*, 1934, **56**, 642; *A.*, 1934, 485.

[25] *Z. physikal. Chem.*, 1932, [*B*], **16**, 19; *A.*, 1932, 459.

[26] *J.*, 1935, 1436, 1487.

[27] *J. Amer. Chem. Soc.*, 1934, **56**, 255; *A.*, 1934, 370.

[28] *Ibid.*, 1932, **54**, 602; *A.* 1932, 458.

Structure of Solid Adsorbing and Catalysing Surfaces.—In earlier Reports reference has been made to H. S. Taylor's theory of surface heterogeneity based on the postulated occurrence of extra-lattice projections or peak areas which are associated with special activity. This important conception of extra-lattice projections has been discussed by a number of workers. O. Schmidt [30] mentions in this connexion G. Tammann and W. Boehme's observation [31] that small particles of metals—*e.g.*, small rods or films of gold, for instance of an order of thickness of 4μ, at 200°—have only a very short life and disappear through sintering, by virtue of differences in vapour pressure, an effect which must be even more intense with extra-lattice projections of molecular dimensions. Again, E. Fajans [32] has shown, and it is a matter of general experience, that a very short sintering period is sufficient to stabilise a nickel surface in such a way that it does not change in activity even on prolonged further exposure to temperatures up to the sintering temperature.

Evidence for the effective uniformity of a metallic catalysing surface has been put forward by E. W. R. Steacie and E. M. Elkin,[33] who have shown that there is no discontinuity at the melting point in the activity of zinc when this metal is used as a catalyst for the decomposition of methyl alcohol between 360° and 440°, from which it is concluded that the whole surface is uniformly active and that the catalytic activity is not limited to a part only; for, if active centres are involved in the catalytic reaction on solid zinc, it would be expected that there would be a sudden and very large drop in the activity at the melting point. The equivalence of the catalysing surface elements has also been discussed by G. M. Schwab,[34] who considers, on reaction-kinetic grounds, that catalysis is carried out by a range of energetically homogeneous points. Further evidence may, moreover, be obtained [35] from the effect of progressive poisoning and of deactivation by heat treatment, and by a re-examination of G. Vavon and A. Husson's work[36] on step-wise deactivation.

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[29] *Z. Elektrochem.*, 1934, **40**, 754; *A.*, 1935, 28.

[30] *Ber.*, 1935, [*B*], **68**, 1098; *A.*, 940.

[31] *Ann. Physik*, 1932, [v], **12**, 820; *A.*, 1932, 452.

[32] *Z. physikal. Chem.*, 1935, [*B*], **28**, 252.

[33] *Proc. Roy. Soc.*, 1933, [*A*], **142**, 457; *A.*, 1934, 38.

[34] *Z. physikal. Chem.*, 1934, **169**, 81; **171**, 421.

[35] E. B. Maxted and G. J. Lewis, *J.*, 1933, 502; E. B. Maxted and V. Stone, *ibid.*, 1934, 26, 672; E. B. Maxted and C. H. Moon, *ibid.*, 1935, 393; E. B. Maxted, *J. Soc. Chem. Ind.*, 1934, **53**, 102T; *A.*, 1933, 680; 1934, 262, 607, 851; 1935, 589.

Although many observations apparently indicate the effective equivalence of the catalysing range of surface elements, yet the extension of this to equivalence throughout the whole range of adsorbing points is bound up with the question as to whether all adsorbing points are equally effective for catalysis. Steacie and Elkin's work on the absence of discontinuity in activity at the melting point of a solid catalyst would appear to show that this is so, at any rate in the case investigated; but this extension is not in conformity with Pease and Stewart's observation[37] of the non-correspondence between the depression of catalytic activity and adsorptive capacity which is caused by partial poisoning; and further investigation is undoubtedly still required. The limited degree of equivalence, namely, that of the catalysing points, is, however, not incompatible with the adlineation theory of Pietsch and Schwab.[38]

Heterogeneous Catalysis.—It is becoming more and more evident that heterogeneous catalytic reactions are processes the mechanism of which is complicated, not only by the presence of a transition state, but also by composite adsorption effects. For this reason, activation energies calculated by applying the simple Arrhenius relationship have little significance, unless the conditions are such that they refer to a dominant stage.

In this connexion, attention may be drawn to an activation mechanism which has been proposed by E. C. C. Baly,[39] according to which the total critical increment required in a heterogeneous catalytic reaction is supplied in two stages. G. H. Bottomley, B. Cavanagh, and M. Polanyi[40] also consider that such reactions take place in two stages, the second being the slower and therefore the rate-determining process. This is suggested, further, in Horiuti and Polanyi's treatment of the part played by nickel or another catalyst in the hydrogenation or hydrogen–deuterium exchange of ethylene or benzene.[41] In any case, a mechanism which involves the formation of an intermediate adsorption complex appears to be generally applicable. A surface may, in exceptional circumstances, promote reaction outside the adsorbed phase, for instance by the initiation of chain reactions.[42] The degree of gaseous chain initiation which was claimed by K. Bennewitz and W. Neumann [43] in ordinary catalytic reactions such as in the hydrogenation of ethylene on platinum appears, however, to be unfounded;[44] and heterogeneous catalytic reactions of the usual type may probably be regarded as being effectively confined to the adsorbed phase.

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[36] *Compt. rend.*, 1922, **175**, 277; *A.*, 1922, ii, 631.

[37] R. N. Pease and L. Stewart, *J. Amer. Chem. Soc.*, 1925, **47**, 1235; *A.*, 1925, ii, 691.

[38] E. Pietsch, A. Kotowski, and G. Berend, *Z. physikal. Chem.*, 1929, [*B*], **5**, 1; *A.*, 1929, 1150; G. M. Schwab and E. Pietsch, *Z. Elektrochem.*, 1929, **35**, 135; *A.*, 1929, 519; G. M. Schwab and L. Rudolph, *Z. physikal. Chem.*, 1931, [*B*], **12**, 427; *A.*, 1931, 919.

[39] *Nature*, 1935, **136**, 146; *A.*, 1084.

[40] *Ibid.*, p. 103; *A.*, 1084; see also J. Horiuti and M. Polanyi, *Proc. Manchester Lit. Phil. Soc.*, 1934, **78**, 50.

[41] *Trans. Faraday Soc.*, 1934, **30**, 1164; *A.*, 1934, 1077.

The relative influence of the various adsorption components on the reaction velocity has continued to receive attention, particularly from the standpoint of the catalytic importance of the slower forms of adsorption. Thus, J. Howard and H. S. Taylor [45] consider that the activated adsorption of ethylene is the rate-determining factor in the hydrogenation of ethylene on catalysts of the oxide type; and P. H. Emmett and S. Brunauer [46] regard the slow adsorption of nitrogen by various ammonia catalysts as being the controlling step in the synthesis. Chief interest is attached to cases where a relatively rapid and a relatively slow adsorption component, each of which constitutes a source of supply of the same molecular species, occur concurrently. M. Polanyi's theory of the mechanism of catalytic hydrogenation [47] requires that the catalytically active adsorption should be not a strong, but an extremely weak, activated adsorption; and, where there are, side by side, a slow activated adsorption, of high apparent activation energy, and a rapid adsorption, of low activation energy, on the same catalyst, the catalysed reaction should, according to the above conception, proceed through the latter and not through the former. An example of this is to be found in the observation of A. J. Gould, W. Bleakney, and H. S. Taylor [48] that the interaction of hydrogen and deuterium at low temperatures takes place far more rapidly than the rate of activated adsorption.

The degree of influence of a dominant adsorbed species, together with the utilisation of the heat of association as a contributory factor towards the activation energy, has been developed by H. zur Strassen [49] and by G. M. Schwab [50] in connexion with the passage of a reaction velocity through a maximum value as the reaction temperature is increased—with subsequent production of a negative temperature coefficient—and as an alternative to ascribing this negative coefficient to a decrease in adsorbed concentration. Thus, in the hydrogenation of ethylene on nickel, the variation of the reaction velocity with temperature is represented by an expression of the form

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[42] See *e.g.*, M. W. Travers, *Nature*, 1935, **136**, 909.

[43] *Z. physikal. Chem.*, 1930, [*B*], **7**, 247; *A.*, 1930, 715.

[44] K. Bennewitz and W. Neumann, *ibid.*, 1932, [*B*], **17**, 457; *A.*, 1932, 818.

[45] *J. Amer. Chem. Soc.*, 1934, **56**, 2259; *A.*, 1935, 28.

[46] *Ibid.*, p. 35; *A.*, 1934, 262.

[47] *J. Soc. Chem. Ind.*, 1935, **54**, 123T; *A.*, 711.

[48] *J. Chem. Physics*, 1934, **2**, 362; *A.*, 1934, 1074.

[49] *Z. physikal. Chem.*, 1934, **169**, 81; *A.*, 1934, 974.

[50] *Ibid.*, 1934, **171**, 421; *A.*, 1935, 441.

$$k = ae^{-\{(E - Q_{H_2}) - Q_{C_2H_4}\}/RT}$$

in which k is the reaction velocity, E the activation energy of the hydrogenation reaction, Q_{H_2} and $Q_{C_2H_4}$ the heats of adsorption of the hydrogen and of the ethylene, and a a factor involving adsorbed concentrations. According to the views of these authors, the reversal takes place at a temperature at which adsorption of the ethylene, together with its heat of adsorption, begins to be an effective factor in the kinetics. A similar treatment has also been applied in connexion with the reversal in the sign of the temperature coefficient in the hydrogenation of crotonic and maleic acids in a dissolved state in the presence of platinum.[51]

While a further examination of the controlling mechanism postulated by zur Strassen and Schwab is obviously needed, since other methods of control are possible, their treatment of these cases of reversal appears both suggestive and—provided that it can be confirmed—capable of wider application. Certainly, without some modification in the Arrhenius equation for these heterogeneous reactions, the calculated values for the activation energy are of rather indefinite significance.

An alternative view to the above aspect of the reversal has been put forward by T. Tucholski and E. K. Rideal.[52] These authors find that hydrogen and deuterium reduce ethylene at equal rates in the high-temperature region,[53] from which it is pointed out that the rate is probably determined by some reaction involving the hydrogen which does not involve a zero-point energy difference; and control by activated migration, probably of hydrogen, is suggested. A further alternative, which Tucholski and Rideal consider less probable, is control by a reaction involving identical energies of activation for the ethylene, the negative temperature coefficient being due to its desorption. R. Klar [54] also observed a reversal in the hydrogenation of ethylene with both isotopes in the presence of an iron catalyst. At temperatures up to about 100°

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[51] *J.*, 1935, 1190; *A.*, 1210.

[52] *Ibid.*, p. 1701.

[53] See R. N. Pease and A. Wheeler, *J. Amer. Chem. Soc.*, 1935, **57**, 1144; *A.*, 938.

[54] *Z. physikal. Chem.*, 1934, [*B*], **27**, 319; *A.*, 1935, 175.

deuterium reacts with ethylene more slowly than hydrogen, but, above this temperature, a more rapid reaction with the heavy isotope took place. With deuterium, the maximum velocity occurred at about 150°, whereas, with hydrogen, reversal took place at about 125°.

Some work has been done on the mode of activation of catalysts by secondary constituents. For instance, an interesting study of the nature of the association between the constituents of a number of two-component catalysts has been made by G. Wagner, G. M. Schwab, and R. Staeger.[55] In cases in which an abnormal increase in catalytic activity—compared with the activity of each of the components separately—occurs, *X*-ray analysis shows evidence for chemical association between the components, in contrast to the occurrence of the lattice structure of each of the components separately in other cases. Thus, CuO,ZnO and CuO,MgO gave diagrams showing no association, whereas CuO,Cr_2O_3 and CuO,Al_2O_3 showed the formation of a new complex with the possibility of new adsorptive properties. Similarly, A. Mittasch and E. Keunecke [56] have obtained evidence, on chemical grounds and as the result of *X*-ray examination, of the formation of mixed crystals of alumina and ferric oxide in the promotion of iron–ammonia catalysts with alumina. These authors infer that one function of the promoter is to inhibit the reduction of the iron oxide. J. Eckell [57] found that the apparent activation energy of an iron oxide catalyst promoted with an increasing concentration of alumina decreased linearly with the alumina concentration up to a content of about 25%, and this was accompanied by a parallel change in the lattice structure.

Of the catalytic reactions which have been studied during the period under review and which possess special general significance, a brief reference may be made to catalysed processes involving deuterium, for which, as would be expected, the same catalysts can be employed as for the lighter isotope. The saturation of ethylene by deuterium in the presence of metallic catalysts has already been noticed. K. Morikawa, W. S. Benedict, and H. S. Taylor [58] have used nickel for the deuterium–hydrogen exchange in methane. J. Horiuti, G. Ogden, and M. Polanyi [59] found that substitution took place on shaking benzene with deuterium in the presence of nickel or platinum; although these substitutions also occur in the absence of a catalyst.[60] The somewhat similar process of exchange

[55] *Z. physikal. Chem.*, 1934, [*B*], **27**, 439; *A.*, 1935, 455.
[56] *Z. Elektrochem.*, 1932, **38**, 666; *A.*, 1932, 1004.
[57] *Ibid.*, p. 918; 1933, **39**, 855; *A.*, 1933, 131, 1253.
[58] *J. Amer. Chem. Soc.*, 1935, **57**, 592; *A.*, 588.
[59] *Trans. Faraday Soc.*, 1934, **30**, 663; *A.*, 1934, 973.
[60] *Nature*, 1934, **134**, 734; *A.*, 1935, 74.

of atoms between water and deuterium may also be catalysed by platinum-black.[61]

In the above review, no attempt has been made to deal with the many catalytic reactions which are of interest principally in relation to the process involved, rather than from a general standpoint, since such catalytic processes are more logically considered in the section appropriate to the reaction in question.

E. B. M.

7. The Physical Basis of Optical Rotatory Power.

The progress which has recently been made towards the elucidation of the problem of the origin of optical rotatory power has culminated during the present year in an important paper by M. Born.[1] Current theories may be divided into two classes, " electronic " and " molecular," but they have a common basis in the theory of coupled vibrators, proposed by M. Born in 1915,[2] according to which a molecule may be represented by a system of electrical particles which are more or less rigidly fixed relative to one another but become polarised (*i.e.*, undergo small displacements) under the influence of an applied electric field, such as the electric vector of a plane-polarised light wave. When one particle is set in vibration, it sends out secondary waves which act on the other particles just as the primary light wave does, and this process is repeated from particle to particle. If the particles are isotropic, rotation of the plane of polarisation can appear as a third-order effect when not less than four of them have taken part in the resonance process, or when two have taken part if they are anisotropic; but only on the condition that the four particles do not lie in the same plane in the former case, and that, in general, the system has no plane or centre of symmetry. This is a mathematical statement of the principle of molecular dissymmetry, but unfortunately, the detailed analysis in the general case is extremely complicated, and involves parameters which are not directly accessible to physical or chemical measurement. Subsequent developments have therefore consisted in the introduction of simplifying assumptions, and the difference between the electronic and the molecular theory lies only in the nature of the simplifications which they involve.

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[61] J. Horiuti and M. Polanyi, *Nature*, 1933, **132**, 819; *A.*, 1934, 17.

[1] *Proc. Roy. Soc.*, 1935, [*A*], **150**, 84.

[2] *Physikal. Z.*, 1915, **16**, 251, 437; *Ann. Physik*, 1918, [iv], **55**, 177. See also M. Born and P. Jordan, " Elementare Quantenmechanik," 1930, 250; M. Born, " Optik," 1933.

(i) W. Kuhn[3] applied the principle of coupling to a molecular model consisting of two *linear* (*i.e.*, completely anisotropic) vibrators which are constrained to move only in directions perpendicular to one another along axes separated by a vertical distance *d* (Fig. 3*a*), the optically active medium being treated as a collection of such models in random orientation. Under these conditions, optical activity is promoted from a third-order to a first-order effect, with a consequent reduction in mathematical complexity. For wave-lengths remote from an absorption band, formulæ are obtained which are identical with those of Drude or of Natanson, but they have the merit of being consistent with the model, whereas W. Kuhn[4] showed that Drude's conception of spiral oscillators does not actually lead to rotatory power at all. Kuhn's model, however, itself needed modification, since the value of *d* derived for it from measurements of circular dichroism (see below) proved in many cases to be incompatible with the known molecular dimensions; but W. Kuhn and K. Bein[5] were able to show that activity of the correct order of magnitude can result so long as the axes of the vibrators are inclined, but not parallel, to one another, and acceptable values of *d* are then obtained when the angle between them is small. Born criticises this model on the ground that " it makes no attempt to reduce *a priori* the dimensions and location of the assumed resonators to other known properties of the molecule." The conception of a *linear* vibrator, also, which implies that the radical to which it corresponds can *never* be polarised in any direction inclined to its one axis, seems remote from the relatively flexible electronic systems which seem to exist in chemical molecules, whilst, in the case of the simplest active molecule with a central asymmetric carbon atom, the presence of four dissimilar radicals seems to call for four vibrators, and the system of two anisotropic resonators must form part of a molecule containing at least four atoms or radicals, since otherwise a plane of symmetry would be possible.[6]

Kuhn's model does not therefore appear to be capable of direct application to the asymmetric carbon atom, but there is a class of compound to which it bears a closer resemblance, *i.e.*, those *spiro*-molecules which, though possessing no asymmetric carbon atom, have no plane of symmetry and can therefore be prepared in optically active forms. Kuhn and Bein [7] selected as an example erythritoldipyruvic acid (I), in which the molecular dissymmetry

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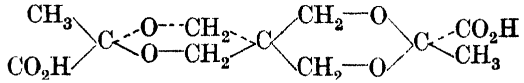
[3] *Z. physikal. Chem.*, 1929, [*B*], **4**, 14; *Trans. Faraday Soc.*, 1930, **26**, 293; *Ber.*, 1930, **63**, 190.

[4] *Z. physikal. Chem.*, 1933, [*B*], **20**, 325. See also M. Born, *Ann. Physik*, 1918, [iv], **55**, 177.

[5] *Z. physikal. Chem.*, 1933, [*B*], **22**, 406.

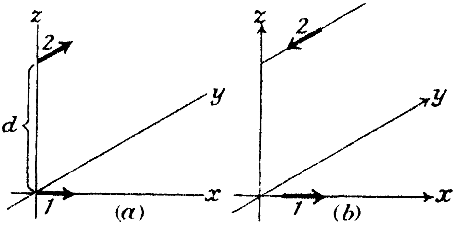
[6] M. Born, *loc. cit.*, ref. (1); T. M. Lowry, *Nature*, 1935, **136**, 191.

(I.)



arises from the fact that the planes containing the two systems $HO_2C—C—CH_3$ must be perpendicular to one another, as is indicated by the dotted lines. If the two carboxyl groups are identified with the two completely anisotropic resonators of the original model (Fig. 3*a*), this reduces to the form of Fig. 3*b*, where the resonators are displaced along their respective axes from the central axis of the model. Kuhn and Bein predicted that the configuration of Fig. 3*b* would be lævorotatory, and they also investigated the absolute configurations of the cobaltioxalates in a similar way,[8] but in neither case were their conclusions in agreement with the general principles now developed by Born.

FIG. 3.



Kuhn achieved more success in the analysis of curves of rotatory dispersion inside an absorption band (the Cotton effect). Experiment shows that, as an absorption band is approached, the rotation rises to a maximum value (+ or —), returns to zero at the centre of the band, and then passes through a second maximum value of opposite sign. This phenomenon was successfully treated by L. Natanson [9] on the basis of Fresnel's fundamental postulate of circular double refraction in an optically active medium and Cotton's demonstration of the corresponding phenomenon of circular dichroism (difference of absorbing power for light circularly polarised in left- and right-handed senses). The contribution of the absorption band to the rotatory dispersion of the molecule (its "partial rotation") can be predicted from a knowledge of the shape of the absorption curve (*i.e.*, its strength f as determined from the area covered, which is $\int \varepsilon . d\nu$ where ε is the molecular extinction coefficient at frequency ν), and of the magnitude of its circular dichroism, $\varepsilon_r \sim \varepsilon_l$, for the measurement of which at ultra-violet wave-lengths W. Kuhn and E. Braun[10] have developed a simple method.

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[7] *Z. physikal. Chem.*, 1934, [*B*], **24**, 335.

[8] *Z. anorg. Chem.*, 1934, **216**, 321.

[9] *Bull. Acad. Sci. Krakow*, 1908, 764; *J. Phys. Radium*, 1909, [iv], **8**, 321. See also Kuhn and Freudenberg, "Handbuch der chemischen Physik," 1932, 8, III, p. 77.

Numerical calculation of partial rotations by Natanson's method demands a knowledge of the relationship between ε and ν inside each absorption band in order that the integral $\int \varepsilon . d\nu$ may be correctly evaluated. Relationships which had been deduced by Natanson on a classical theory of damped oscillations were found to be inadequate, but Kuhn and Braun[11] obtained more success with an empirical exponential expression of a type which had been suggested by J. Bielecki and V. Henri.[12] This expression has been further modified by T. M. Lowry and H. Hudson[13] and the partial rotations then deduced give excellent agreement with the curves obtained experimentally. Striking examples of the application of this method of treating the Cotton effect are the analysis by W. Kuhn and H. L. Lehmann[14] of a very curious curve of rotatory dispersion obtained from β-octyl nitrite, and the demonstration by H. Hudson, M. L. Wolfrom, and T. M. Lowry[15] that the rotatory power of tetra-acetyl μ-arabinose is contributed entirely by the ultra-violet absorption band of the carbonyl radical, whilst the partial rotations from the asymmetric carbon atoms entirely cancel one another.

(ii) S. F. Boys,[16] in contrast to Kuhn, based his analysis on the simplest chemical model which can show optical activity, an asymmetric carbon atom surrounded by four different radicals. This is a return to Born's system of four isotropic resonators arranged tetrahedrally; but, instead of making use of the results which had already been established, Boys attempted to calculate the forced vibrations of the resonators directly, expressing their polarisabilities in terms of their refractivities instead of taking into account their characteristic frequencies. This method is involved, and the results do not entirely agree with the rigorously established formulæ of the general theory. They lead to an expression for the rotatory power of the molecule in terms of the product of the refractivities of the four radicals, and of a complex function of the linear dimensions of the molecule which he deduced approximately from the "atomic" radii of the radicals, assuming them to be close-packed spheres. A similar result was obtained, by different reasoning, by R. de Mallemann.[17] Since the characteristic frequencies of the radicals are only involved implicitly in their refractivities [which may be expressed in the form $a_k/(\lambda^2 - \lambda_k^2)$, a_k being a constant and λ_k the wave-length characteristic of the kth absorption frequency], it follows that the rotatory power and refractive index should depend on wave-length in the same way: but this conclusion must be invalid,[18] since in the case of refractive dispersion the constants a_k are always positive, whereas in the case of rotatory dispersion some of them may be negative, and the general theory requires that $\Sigma a_k = 0$, a result also obtained by Kuhn; and experiment actually shows that absorption bands which give only a tiny contribution to the refractive index often contribute very largely indeed to the rotatory power of a molecule. At wave-lengths in the visible spectrum, Boys's formula leads to values for the specific rotations of simple alcohols and amines which are in excellent agreement with experiment, but, as is to be expected, it does not give satisfactory values for their rotatory dispersions; nor can it explain the Cotton effect, since the reversal of sign in the refractivity of the chromophoric radical, which is necessary to account for the observed reversal of the sign of the rotatory power at the centre of its absorption band, does not occur.[19] On the other hand, for a given arrangement of the four radicals, Boys's analysis leads directly to an unambiguous prediction of the *sign* of the rotation, and he specified the absolute configurations of simple optically active molecules such as amyl alcohol.

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[10] *Z. physikal. Chem.*, 1930, [*B*], **8**, 445. [11] *Ibid.*, p. 281.

[12] *Physikal. Z.*, 1913, **14**, 516. [13] *Phil. Trans.*, 1933, [*A*], **232**, 131.

[14] *Z. Elektrochem.*, 1931, **37**, 549; *Z. physikal. Chem.*, 1932, [*B*], **18**, 32.

[15] *J.*, 1933, 1179. W. C. G. Baldwin, M. L. Wolfrom, and T. M. Lowry have also found optical cancellation in penta-acetyl μ-fructose; *J.*, 1935, 696.

[16] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 655.

(iii) Born [20] has now reshaped his general theory in such a way as to make it available immediately for chemical purposes. He starts from the simple model of the tetrahedral molecule, but, for technical reasons, he assumes the four resonators to be *slightly* anisotropic on the ground that theory shows that such anisotropy will inevitably occur as a result of the coupling forces even if the resonators are initially isotropic. At present, he considers only those wave-lengths which are remote from an absorption frequency, since the complex (and often diffuse) band systems of real molecules are beyond the scope of the method of analysis employed, and any formulæ which represent the variation of rotatory power inside absorption bands must at best be semi-empirical in character;

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[17] *Compt. rend.*, 1925, **181**, 298; *Trans. Faraday Soc.*, 1930, **26**, 281.

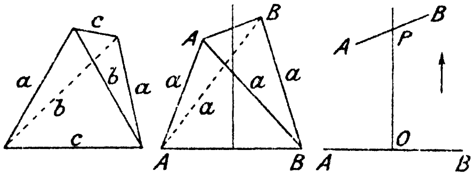
[18] M. Born, *loc. cit.*, ref. (1).

[19] T. M. Lowry and C. B. Allsopp, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 317.

[20] *Loc. cit.*, ref. (1).

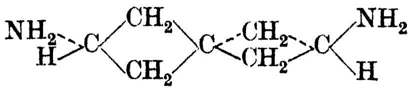
but with this restriction, he deduces a simple formula for rotatory power which depends only on the frequencies and strengths of the four resonators and on their arrangement in space. In general, this formula is only valid when no two of the resonators are equal, but there is a limiting case where it still holds even when two pairs of them are the same, *viz.*, when the faces of the tetrahedron have the form of congruent triangles (Fig. 4*a*). Still greater simplification results when these two pairs are so arranged that the lines joining them are perpendicular to one another and to the line joining the centres of the corresponding edges of the tetrahedron (Fig. 4*b*). This, of course, is exactly the configuration of the erythritoldipyruvic acid molecule considered by Kuhn, but whereas Kuhn's treatment only involved two of the four radicals (the carboxyl groups), Born's formula takes account of all four of them. The formula does not implicitly include the sign of the rotation for a given molecular configuration, but this can be deduced from the general theory : " The rotation of the plane of the polarisation is represented by the same screw motion which makes the two atom pairs coincide, if one pair is moved along the line connecting the centres of the pairs." The model of Fig. 4*c* is therefore lævorotatory, although the screw is right-handed, since chemists specify the sign of rotation when *facing* the on-coming light. This conclusion is the opposite of that reached by Kuhn for the *spiro*-acid ; the dispersion factor in Born's formula, however, is identical with that obtained by Kuhn. Born's formula was used to calculate the rotatory power of diamino*spiro*heptane (II),[21] in which the dissymmetry arises from

FIG. 4.



(*a*) (*b*) (*c*)

(II.)



$$\begin{matrix}NH_2\\H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}NH_2\\H\end{matrix}$$

the spatial arrangement of the hydrogen atoms and amino-groups, which thus correspond with the pairs of resonators AB, AB in the model. The parameters in the formula (the distances A–B and O–P in Fig. 4*c*, and the characteristic frequencies of the hydrogen atom and of the amino-radical) are not known, but appropriate guesses lead to a value $[M]_{5461} = 30°$, which is in good agreement with experiment.

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[21] Resolved by (Sir) W. J. Pope and S. E. Janson, *Chem. and Ind.*, 1932, **51**, 316.

Born has provided chemists with a physical theory of optical rotatory power which has a sound mathematical basis, and, when sufficient experimental accuracy in the determination of the various parameters is attainable, will make it possible to predict the absolute rotatory powers of molecules of known configuration; but the achievement of such accuracy will always be difficult, for Born's formula involves the eighth power of the molecular dimensions and the sixth power of the frequency and the square of the strength of absorption bands which lie in a region of the spectrum where measurements are by no means simple. For the moment, therefore, as T. M. Lowry has pointed out,[22] the chief importance of Born's work is that it can be applied to the prediction of the relative magnitudes of the rotatory powers of related compounds, as functions of three pairs of their fundamental physical constants, when the experimental errors in the parameters may be of much less importance.[23]

C. B. A.

8. DIPOLE MOMENTS AND VALENCY ANGLES.

In addition to being used in the qualitative determination of molecular structures,[1] dipole moments have been applied for the purpose of calculating valency angles. The fundamental assumptions involved are the constancy of bond moments, which are supposed to act along the direction of the valency bonds, and their strict vector additivity without any interaction effects of one moment on another.[2] If the constituent bond moments, either singly or in the form of group moments, and the total dipole moment of a compound are known, then clearly it should, in general, be possible to calculate the angles between certain individual moments, *i.e.*, between the corresponding covalency linkages. One of the simplest applications is to determine the angles between the *o*-, *m*-, and *p*-directions, respectively, in the benzene ring; if this is a plane regular hexagon, these angles should be 60°, 120°, and 180°, respectively. As far as the *m*- and *p*-positions are concerned, the results are in agreement with expectation, but the moments of *o*-substituted compounds frequently imply that the angle between the valency directions is greater than 60°.[3] This discrepancy, known as the "ortho-effect," has been attributed to actual distortion of the molecule resulting from the size of the substituent groups,[4] or to mutual interaction between the two dipoles,[5] so that the assumption of the constancy of the group moments—or of their strict vector additivity—taken as equal to the values for the corresponding monosubstituted benzene compounds, is no longer valid. It is probable that both factors are operative : measurements of the C–I and I–I distances in *o*-di-iodobenzene by the electron-diffraction method indicate that the angle between the two C–I bonds is at least 68°,[6] and may be as high as 80°.[7] A similar distortion of the molecule appears to occur in the *peri*-substituted naphthalene derivatives.[6, 8] There is little doubt, however, that, in addition, interaction between groups occurs :[9] in some cases this is probably due to simple inductive polarisation, but in others it is connected with the permanent electromeric, *i.e.*, mesomeric,[10] effect in the molecule.[11] It is the error in the calculations resulting from the presence of such an effect which led to the conclusion [12] that the moment of the $>$C–CN system does not act in the direction of the C–C bond; there is now little doubt that this view is incorrect.[13]

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[22] *Nature*, 1935, **136**, 191.

[23] Reference must also be made to the appearance of T. M. Lowry's "Optical Rotatory Power" (Longmans, 1935), which contains a comprehensive detailed account of the development and significance of this recent work.

[1] *Ann. Reports*, 1931, **28**, 387.

[2] (Sir) J. J. Thomson, *Phil. Mag.*, 1923, **46**, 513; *A.*, 1923, ii, 682; see also K. Höjendahl, *Physikal. Z.*, 1929, **30**, 391; *A.*, 1929, 980.

In general, when two identical or different groups, or when three identical groups, are attached to the same atom, it is possible to determine the valency angles, provided the individual group moments and the total moment of the compound are available.[14] For example, the angles between the C–X links in CH_2X_2 and CHX_3, where X is a halogen, have been calculated in this manner; [14,15] an allowance of 0·4D for the moment of the C–H bonds can be made, or alternatively, it may be assumed that the value for the C–X bond is equal to the moment of CH_3X, the neglect of the C–H moment resulting in a cancellation of the errors involved. The angles for methylene chloride and for chloroform were found to be about 130° and 116°, respectively, in good agreement with those obtained from *X*-ray diffraction measurements on the vapours,[16] *viz.*, $124° \pm 6°$ and $116° \pm 3°$. Analogous observations of electron scattering show, however, that the latter values are probably in error,[17] and that the valency angles in the two compounds mentioned are $111° \pm 2°$, a result in agreement with calculations based on wave mechanics.[18] It is evident that in the chloromethanes there is considerable mutual interaction of the dipoles so that the C–Cl bond moments may be reduced by as much as 30%.[19] Similar interaction probably occurs in the other halogenomethanes; no measurements of interatomic distances in the vapours, from which valency angles can be calculated, have been reported, but it is probable that, as the size of the halogen increases,[20] the valency angles become greater than the tetrahedral value, although it is unlikely they will prove to be as large as those —134° and 140° for methylene bromide and iodide, respectively—calculated from dipole moments.[14] In spite of statements to the contrary, it now appears that inductive effects are also operative in *cis*-dichloroethylene: the presence of a double bond in this molecule may, however, be a special contributive factor.[21]

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[3] C. P. Smyth and S. O. Morgan, *J. Amer. Chem. Soc.*, 1927, **49**, 1030; *A.*, 1927, 611; E. Bergmann and L. Engel, *Z. physikal. Chem.*, 1930, [*B*], **8**, 111; *A.*, 1930, 979; E. Bergmann, L. Engel, and S. Sándor, *ibid.*, **10**, 106; *A.*, 1930, 1501.

[4] C. P. Smyth and S. O. Morgan, *loc. cit.*

[5] H. M. Smallwood and K. F. Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919; *A.*, 1930, 84.

[6] H. de Laszlo, *Trans. Faraday Soc.*, 1934, **30**, 892.

[7] S. B. Hendricks, L. R. Maxwell, V. L. Mosley, and M. E. Jefferson, *J. Chem. Physics*, 1933, **1**, 549; *A.*, 1934, 17.

[8] A. Weissberger, R. Sängewald, and G. C. Hampson, *Trans. Faraday Soc.*, 1934, **30**, 884; *A.*, 1934, 1157.

[9] G. C. Hampson and L. E. Sutton, *Proc. Roy. Soc.*, 1933, [*A*], **140**, 562; *A.*, 1933, 766; H. Poltz, O. Steil, and O. Strasser, *Z. physikal. Chem.*, 1932, [*B*], **17**, 155; *A.*, 677; E. G. Cowley and J. R. Partington, *J.*, 1935, 604; *A.*, 809; K. Höjendahl, *loc. cit.*

[10] C. K. Ingold, *J.*, 1933, 1120; *A.*, 1933, 1151.

[11] G. M. Bennett, *Ann. Reports*, 1929, **26**, 132; G. C. Hampson and L. E. Sutton, *loc. cit.*; G. M. Bennett and S. Glasstone, *Proc. Roy. Soc.*, 1934, [*A*], **145**, 71; *A.*, 1934, 831.

[12] E. Bergmann and M. Tschudnovski, *Z. physikal. Chem.*, 1932, [*B*], **17**, 116; *A.*, 1932, 677.

[13] A. Weissberger and R. Sängewald, *J.*, 1935, 855; *A.*, 976; cf. also R. P. Cook and P. L. Robinson, *ibid.*, p. 1001; *A.*, 1064.

When one or more phenyl groups are attached to a central atom, valency angles may be calculated by making use of the fact that in the *p*-position to the point of attachment the moment of a group such as a halogen, CN, NC, CH_3, or NO_2 acts along the axis of the benzene ring. The dipole moment μ of a compound $C_6H_5—A\diagup^{B}$ is determined by the bond moments of $C_6H_5—A$ (μ_1) and of A—B (μ_2), and by the valency angle (θ), which are related by the usual equation $\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta$, the correct signs being used for the directions of the individual moments.[2] Another equation connecting μ_1, μ_2, and θ can be obtained from the measured moment of the compound *p*-$X{\cdot}C_6H_4{\cdot}AB$, the $X—C_6H_4$ bond moment, assumed equal to the moment of the compound C_6H_5X, acting in the line of the $C_6H_4—A$ bond. In order to calculate θ, it is necessary to know the value of the bond moments μ_1 and μ_2, or to be able to express μ_1 as a function of μ_2; for practical purposes the latter condition is best satisfied by making μ_1 and μ_2 equal, *i.e.*, B is also a phenyl group, and the compounds examined are diphenyl derivatives, $C_6H_5{\cdot}A{\cdot}C_6H_5$. By using either the moment of a monosubstituted compound, *viz.*, *p*-$X{\cdot}C_6H_4{\cdot}A{\cdot}C_6H_5$, or that of a *pp'*-disubstituted derivative, *viz.*, *pp'*-$X{\cdot}C_6H_4{\cdot}A{\cdot}C_6H_4{\cdot}X$, independent values of the valency angle can be obtained; in the latter case, however, two solutions are possible, so that the result is not entirely free from uncertainty.

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[14] G. C. Hampson and L. E. Sutton, *loc. cit.*, ref. (9).

[15] E. Bergmann, L. Engel, and S. Sándor, *loc. cit.*, ref. (3); E. Bergmann, L. Engel, and H. A. Wolff, *Z. physikal. Chem.*, 1932, [*B*], **17**, 81; *A.*, 1932, 677; see also F. R. Goss, *J.*, 1934, 1467; *A.*, 1934, 696.

[16] L. Bewilogua, *Physikal. Z.*, 1931, **32**, 265; *A.*, 1931, 788.

[17] R. Wierl, *Ann. Physik*, 1931, **8**, 521; *A.*, 1931, 665; L. E. Sutton and L. O. Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473.

[18] W. G. Penney, *Trans. Faraday Soc.*, 1935, **31**, 734; *A.*, 810.

[19] L. E. Sutton and L. O. Brockway, *loc. cit.*

[20] Cf. C. P. Smyth and H. E. Rogers, *J. Amer. Chem. Soc.*, 1930, **50**, 222; *A.*, 1930, 1093.

[21] G. C. Hampson and L. E. Sutton, *loc. cit.*, ref. (9), p. 565; see also E. C. E. Hunter and J. R. Partington, *J.*, 1931, 2062; 1932, 2819; *A.*, 1931, 1113; 1932, 210.

Several fundamental assumptions are involved in these calculations : (*a*) that the dipole moment of a compound is strictly the vector sum of the constituent bond or group moments, (*b*) that the valency angle of A remains unchanged by the introduction of the substituent X in the *p*-position of the phenyl group, and (*c*) that there is no interaction between X and the group AB, *e.g.*, $A{\cdot}C_6H_5$. The first assumption is implicit in all calculations involving bond moments, and the second is reasonably probable, except in so far as substitution in two benzene nuclei may result in some repulsion,[22] but the third assumption requires further consideration. A test for interaction between groups is to calculate from the moments of $C_6H_5{\cdot}A{\cdot}B$, C_6H_5X, and *p*-$X{\cdot}C_6H_4{\cdot}A{\cdot}B$, by means of a simple vector triangle, or the equivalent equation, the so-called " characteristic angle," ϕ,[23] between the resultant moment of $C_6H_5{\cdot}A{\cdot}B$ and the axis of the benzene ring passing through A; for a series of substituents X, the value of ϕ should remain unchanged. It was at one time claimed that ϕ was in fact constant for a number of substituted anisoles and anilines,[14, 22] except when the molecule contained groups having large and opposed electromeric effects.

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[22] E. Bergmann and M. Tschudnovski, *Z. physikal. Chem.*, 1932, [*B*], **17**, 107; *A.*, 1932, 677.

[23] E. Bergmann, L. Engel, and S. Sándor, *ibid.*, 1930, [*B*], **10**, 397; *A.*, 1931, 23.

As far as the anisoles are concerned, the apparent constancy of ϕ was shown to be due to the use of incorrect dipole moments; the actual values of the angle for different *p*-substituents follow the polar sequence CH_3, F, Cl, Br, I, and NO_2, and a similar variation probably occurs with the corresponding *p*-substituted anilines. There is little doubt that interaction occurs between the groups X and OCH_3 in the anisoles; this does not appear to be due to inductive effects, but to a permanent polarisation of the mesomeric type transmitted through the conjugated system of single and double bonds in the benzene ring.[24] The same type of interaction appears to occur in all compounds in which a phenyl group is attached to oxygen, sulphur, or nitrogen. For the phenols, the value of ϕ, with X = CH_3, Cl, or Br, appears to be constant,[25] and hence it has been claimed that there is here no evidence for interaction;[26] in view of the fact that *p*-chloro- and *p*-bromo-phenol are virtually one case, and of the very small difference between the moments of phenol (1·56D) and *p*-cresol (1·57D), which leads to considerable uncertainty in the calculation of ϕ, the evidence for the constancy of this angle is very slight.

The methods described above for determining valency angles in diphenyl derivatives have been used to calculate the oxygen and the sulphur angle in diphenyl ethers and diphenyl sulphides,[14, 22, 23, 27] but in view of the existence of interaction moments of considerable, although unknown, magnitude, the results are of no direct value.[24, 26] An examination of the errors in the calculated angles, as a consequence of this interaction moment, supposed to act along the axis of the benzene ring passing through the *p*-positions occupied by A and the substituent X, shows [28] that in certain cases, *e.g.*, nitro- and bromo-diphenyl ethers, the errors in the two independent values of θ obtained from mono- and di-substituted compounds are of opposite sign; *i.e.*, one is greater and the other less than the true value. With other compounds, *e.g.*, ditolyl ethers, the errors are both in the same direction. If these limitations are borne in mind, and allowance is made for possible errors in observation and for solvent effects, for atom polarisation, and for the fact that the interaction moment operative along each benzene ring axis in a disubstituted ether may be less than the value for a mono-substituted derivative, an examination of the available data for various substituted diphenyl ethers leads to the conclusion that in these compounds the oxygen valency angle [26] is 128° ± 4°. This result is in harmony with the fact that diphenylene dioxide has zero moment, so that the molecule must be planar, and consequently the minimum oxygen valency angle in compounds of this type must be 120°; [29] it also agrees with the calculations of deviation moments, which necessitate a valency angle greater than the tetrahedral value in diphenyl ethers, in order to yield a consistent set of results.[30] It is of interest to note that the new calculations imply an interaction moment of about 0·7D for the nitro-group, 0·25D for bromine, and 0·1D for the methyl group, acting along the axis of the benzene ring, in substituted diphenyl ethers. Electron-diffraction measurements indicate an angle of 118° ± 3° in *pp'*-di-iododiphenyl ether.[31]

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[24] G. M. Bennett, *Trans. Faraday Soc.*, 1934, **30**, 853; *A.*, 1934, 1157; G. M. Bennett and S. Glasstone, *loc. cit.*, ref. (11).

[25] H. L. Donle and K. A. Gehrckens, *Z. physikal. Chem.*, 1932, [*B*], **18**, 316; *A.*, 1932, 984.

[26] L. E. Sutton and G. C. Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945; *A.*, 1056.

[27] C. P. Smyth and W. S. Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230; *A.*, 1932, 984; G. C. Hampson, R. H. Farmer, and L. E. Sutton, *Proc. Roy. Soc.*, 1933, [*A*], **143**, 147; *A.*, 1934, 131.

[28] G. C. Hampson, *Trans. Faraday Soc.*, 1934, **30**, 858; G. C. Hampson *et al.*, *loc. cit.*; L. E. Sutton and G. C. Hampson, *loc. cit.*, refs. (9) and (26).

The data for diphenyl sulphides are not so extensive as for the ethers, but the application of the limitations mentioned above to the available measurements leads to a value [26] of 113° ± 3° for the sulphur valency angle. The appreciable dipole moment of thianthren, about 1·5D, indicates that in this compound the valency angle of the sulphur atom must be less than 120°; [32] using the moment for the C_6H_5—S bond, estimated from measurements on diphenyl sulphide, the actual angle may be calculated to be about 110°.[33] An angle of 110—120° is of the order proposed for the sulphur atom in the thiocyanate group [34] and in alkyl sulphides [35] to account for the dipole moments of various compounds.

It is perhaps surprising that the oxygen angle in the diphenyl ethers is markedly greater than the corresponding angle in other oxygen compounds; for instance, in water the value as determined from spectroscopic measurements[36] is about 105°, and in dimethyl ether the angle has been calculated as 118° from the Raman spectrum[37] and as 111° ± 4° from electron-diffraction measurements.[38] By assuming the moment of the C–O link to be the same in dimethyl ether as in ethylene oxide, in which the oxygen angle is determined by the known dimensions of the oxygen and the carbon atom, the angle in the ether has been calculated[39] to be 115° ± 7°; the objection that the inductive effect of one C–O bond on the other may be different in the two compounds considered[40] does not appear to apply. The angle of 110° in dimethyl ether deduced by the "shadow area" method[41] should not be quoted as evidence, since an application of the same principle led to the conclusion that the Kaufler formula was applicable to diphenyl.[42] The natural valency angle of oxygen in water and in the simple ethers, and also in chlorine monoxide and oxygen fluoride,[38, 43] appears to be slightly less than the tetrahedral value, whereas in diphenyl ethers and related compounds it is 120° or greater; unless the result is due to a misinterpretation of the dipole moments, which appears improbable, some reason for this discrepancy must be sought. The important suggestion has been made[26] that in diphenyl ethers resonance occurs between the normal molecule (I) and two possible excited states (II):

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[29] G. M. Bennett, D. P. Earp, and S. Glasstone, *J.*, 1934, 1179; *A.*, 1934, 1058.

[30] G. M. Bennett and S. Glasstone, *loc. cit.*, ref. (11), p. 76.

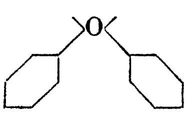
[31] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Physics*, 1935, **3**, 699.

[32] E. Bergmann and M. Tschudnovski, *Ber.*, 1932, **65**, 457; *A.*, 1932, 507; W. S. Walls and C. P. Smyth, *J. Chem. Physics*, 1933, **1**, 337; *A.*, 1934, 12; G. M. Bennett and S. Glasstone, *J.*, 1934, 128; *A.*, 1934, 349.

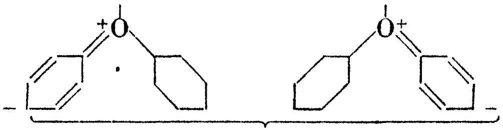
[33] L. E. Sutton and G. C. Hampson, *loc. cit.*, ref. (26), p. 951; cf. also G. M. Bennett, *loc. cit.*, ref. (24), p. 858.

[34] E. C. E. Hunter and J. R. Partington, *J.*, 1932, 2825; *A.*, 1933, 210.

[35] K. A. Jensen, *Z. anorg. Chem.*, 1935, **225**, 97; see, however, E. C. E. Hunter and J. R. Partington, *J.*, 1932, 2812; *A.*, 1933, 210.



(I.)



(II.)

The observations of Pauling and his co-workers[44] indicate as an empirical fact that, when resonance occurs between different possible structures of a molecule, the actual dimensions within the molecule approach more closely the values for the form having the greater radial force constants; *i.e.*, the molecular configuration will favour distances and angles required by double bonds over those necessitated by single linkages. In the diphenyl ethers, therefore, resonance between (I) and either form of (II) will result in a tendency towards an oxygen valency angle of 125° 16′, the usual value between a single and a double bond attached to a tetrahedral atom, instead of the normal angle between two single linkages. The same factor should be operative, to some extent, in phenols and phenolic ethers. If the two benzene rings in diphenyl ether are to lie in one plane, it would be necessary for the oxygen valency angle to be widened to a value lying between 123° and 145°, according as an allowance of 0—0·5 Å. was made for an envelope[45] around the hydrogen atoms in the *o*-positions to represent the repulsion of the electrons. The possibility of this factor influencing the measured value of the valency angle has been considered,[46] and there is reason to believe that the resonance mentioned above may favour a configuration in which the two benzene rings are coplanar.

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[36] R. Mecke, *Z. Physik*, 1933, **81**, 313; *A.*, 1933, 445; see also E. F. Barker and W. W. Sleator, *J. Chem. Physics*, 1935, **3**, 660.

[37] N. G. Pai, *Indian J. Physics*, 1934, **9**, 121; *A.*, 1935, 283.

[38] L. E. Sutton and L. O. Brockway, *loc. cit.*, ref. (17).

[39] G. M. Bennett, *loc. cit.*, ref. (24); see also N. G. Pai, *loc. cit.*, ref. (37).

[40] L. E. Sutton and G. C. Hampson, *loc. cit.*, ref. (26), p. 953.

[41] W. A. Hare and E. Mack, *J. Amer. Chem. Soc.*, 1932, **54**, 4272; *A.*, 1933, 11.

[42] E. Mack, *ibid.*, 1925, **47**, 2468; *A.*, 1925, 1124.

[43] H. Boersch, *Monatsh.*, 1935, **65**, 311; *A.*, 687; see also J. S. Allen and H. Hibbert, *J. Amer. Chem. Soc.*, 1934, **56**, 1398; *A.*, 1934, 831; M. M. Otto, *ibid.*, 1935, **57**, 693; *A.*, 1192; C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc.*, 1933, [*A*], **142**, 129; *A.*, 1933, 1228.

[44] *E.g.*, L. Pauling, *Proc. Nat. Acad. Sci.*, 1932, **18**, 293; also L. E. Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789; *A.*, 1934, 1156.

The normal valency angle of sulphur appears to be definitely less than that of oxygen; analysis of the Raman and infra-red spectra of hydrogen sulphide leads to an angle of 90°[47] or 92° 20′,[48] and a value of 100° has been proposed for dimethyl sulphide, based on its Raman spectrum.[37] The angle of 113° ± 3° for diphenyl sulphide, obtained from measurements of dipole moments,[26] may therefore indicate resonance of a similar type to that postulated for the diphenyl ethers. Nothing is known of the value to be expected for the angle between a single and a double bond attached to sulphur,[48a] but owing to the fact that the radius of the sulphur atom is greater than that of oxygen, a smaller valency angle would accommodate two benzene rings in one plane.

The principles used for calculating valency angles in compounds of the type $C_6H_5{\cdot}A{\cdot}C_6H_5$ can also be applied in cases where other atoms or groups are attached to the atom A, provided the moment of the compound still lies along the axis of symmetry of the molecule, *e.g.*, diphenylmethane,[49] benzophenone,[50] diphenylsulphone,[51] αα-diphenylethylene derivatives,[52] and ααγγ-tetraphenylallene.[53] In diphenylmethane and diphenylsulphone there is no possibility of resonance, so that the angle between the phenyl groups is close to the tetrahedral value, any small deviations being attributable either to experimental error, to the influence of mutual induction on the bond moments, or to steric effects; with benzophenone and αα-diphenylethylene the corresponding angles are about 130°, and in both cases resonance, which should result in the angle being greater than the tetrahedral value, is theoretically possible. In the αα-diphenylallene compounds the angle between the valencies joining the phenyl groups to the carbon atom is found to be 119°; this increase over the tetrahedral angle is in conformity with the Thorpe–Ingold valency-deflexion hypothesis, but it might also be accounted for by resonance.

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[45] N. V. Sidgwick, *Ann. Reports*, 1932, **29**, 70.

[46] *Idem*, *ibid.*, p. 72; C. P. Smyth and W. S. Walls, ref. (27), p. 3238.

[47] A. Dadieu and K. W. F. Kohlrausch, *Physikal. Z.*, 1932, **33**, 165; *A.*, 1932, 320.

[48] P. C. Cross, *Physical Rev.*, 1935, **47**, 7.

[48a] See, however, P. C. Cross and L. O. Brockway, *J. Chem. Physics*, 1935, **3**, 821.

[49] E. Bergmann, L. Engel, and H. A. Wolff, *loc. cit.*, ref. (15); G. C. Hampson, R. H. Farmer, and L. E. Sutton, *loc. cit.*, ref. (27).

[50] E. Bergmann, L. Engel, and H. Meyer, *Ber.*, 1932, **65**, 446; *A.*, 1932, 506; L. E. Sutton and G. C. Hampson, *loc. cit.*, ref. (26), p. 955; see also O. Fuchs and H. L. Donle, *Z. physikal. Chem.*, 1933, [*B*], **22**, 1; *A.*, 1933, 888; O. Hassel and E. Næshagen, *ibid.*, 1929, [*B*], **4**, 217; *A.*, 1929, 275.

[51] E. Bergmann and M. Tschudnovski, *loc. cit.*, ref. (32).

A similar method to that adopted for diphenyl compounds can be applied to triphenyl derivatives [14] in which the resultant moment of the molecule acts along its axis of symmetry; for triphenylmethane and triphenylchloromethane the angle between the three phenyl groups has been calculated from dipole-moment data [54] to be, as expected, about 110°. The method is, theoretically, available for triphenylamine, but the requisite measurements have not yet been made. The application of a similar principle to the determination of the nitrogen valency angle in triethanolamine [55] appears to be open to criticism, since no allowance has been made in the calculations for the possibility of free rotation about the N—C and C—O linkages.

When the direction of the moment of an unsubstituted diphenyl compound is not collinear with the bisector of the angle between the axes of the benzene rings, but is equally inclined to both of them, as in diphenylsulphoxide or diphenylamine, it is possible to calculate the angle between the phenyl groups from a knowledge of the moments of the unsubstituted molecule and of a mono-*p*-substituted and a di-*pp*′-substituted derivative containing the same substituent.[14] An alternative value of the angle can be obtained if, instead of the last two moments, the values are known for two di-*pp*′-compounds, each with two identical groups, which are as widely different as possible in the two compounds. Both these methods have been used to determine the configuration of diphenylsulphoxide,[56] with the result that the angle between the two

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[52] E. Bergmann, L. Engel, and H. Meyer, *loc. cit.*, ref. (50).

[53] E. Bergmann and G. C. Hampson, *J.*, 1935, 989; *A.*, 1115.

[54] E. Bergmann, L. Engel, and H. A. Wolff, *loc. cit.*, ref. (15).

[55] J. N. Pearce and L. F. Berhenke, *J. Physical Chem.*, 1935, **39**, 1005.

[56] G. C. Hampson, R. H. Farmer, and L. E. Sutton, *loc. cit.*, ref. (27), p. 164.

C_6H_5—S bonds has been found to be 112° ± 8°; the close agreement between this and the tetrahedral angle is in harmony with the fact that from the chemical properties of the sulphoxide group there is no expectation of resonance of the type to which the widening of the valency angle in diphenyl ether has been attributed.[26]

The alternative procedure for determining the valency angle in a compound of the type C_6H_5—A—B, involving a knowledge of one of the group moments (p. 129), has been applied to compounds having the general formula $C_6H_5{\cdot}CH_2X$, *viz.*, benzyl chloride, bromide, and cyanide. In these substances no appreciable interaction between the CH_2X group and other groups substituted in the *p*-position is to be expected, and so the dipole-moment method should give reliable results. The assumption is made that the resultant moment of the unsubstituted compound, $C_6H_5{\cdot}CH_2X$, acts in the direction of the C—X bond; this is equivalent to assuming that the bond moments of C—H, in the methylene group, and of C_6H_5—C are zero, so that the only effective moment in the molecule is that of the C—X linkage, the value of which is equal to the measured dipole moment of the compound. These postulates are not strictly justifiable, but it is probable that the errors involved effectively cancel one another. From the moments of the benzyl compounds and of a number of *p*-substituted derivatives, the angle between the C_6H_5—C and C—X bonds was calculated as 114—119°: the departure from the tetrahedral angle is regarded as being no more than the probable errors involved in the determination.[57] In the benzyl compounds no resonance, of the kind already considered, is to be anticipated, so that there should be no widening of the valency angle.[58]

Attempts have been made to estimate the oxygen angle in anisole on the assumption that the moment of the O—CH_3 bond is the same as in dimethyl ether;[59] the values of 140—150° obtained in this manner are undoubtedly in error, because of group-interaction effects in the *p*-substituted anisoles, the moments of which are required for calculating the valency angle.[25, 60] A similar difficulty arises in connexion with the oxygen angle in phenol itself and in other phenolic ethers, but no dipole method appears available at present for overcoming it.

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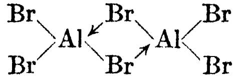
[57] C. P. Smyth and W. S. Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 1854; *A.*, 1932, 794.

[58] See, however, J. M. A. de Bruyne, R. M. Davis, and P. M. Gross, *ibid.*, 1933, **55**, 3936; *A.*, 1933, 1230.

[59] G. C. Hampson *et al.*, *loc. cit.*, ref. (27); see also C. P. Smyth and W. S. Walls, *loc. cit.*, ref. (27), p. 3237.

[60] G. M. Bennett and S. Glasstone, *loc. cit.*, ref. (11); L. E. Sutton and G. C. Hampson, *loc. cit.*, ref. (26).

The dipole moment of 2·13D for hydrogen peroxide was at first attributed[61] to its having the structure $\overset{H}{\underset{H}{}}{>}O{\rightarrow}O$, but it was shown later[62] that the result was in harmony with the ordinary formula H·O·O·H, on the assumption that the oxygen valency angle is tetrahedral and that there is free rotation of the OH groups about the O—O axis. From considerations of wave mechanics,[63] however, it appears that free rotation is unlikely, although spectroscopic considerations indicate the formula H·O·O·H to be the correct one. It is concluded that the two OH groups, which are stationary, are *not* coplanar, and that the two H·O—O planes in the molecule are inclined at an angle of about 100° to one another. The calculations indicate that the oxygen valency angle is also about 100°, and these two values lead to a dipole moment of 2·0D, compared with the observed 2·13D, based on the assumption that the O—H bond moment is the same as in water, and that in the latter substance the oxygen angle[36] is 105°. Similar application of wave-mechanical methods[63] to the hydrazine molecule indicates that it has a structure analogous to that of hydrogen peroxide; the nitrogen valency angle is about 110°, and the two planes containing nitrogen atoms and bisecting one of the two $N{<}\overset{H}{\underset{H}{}}$ angles are perpendicular to one another. From the known dipole moment of ammonia and the dimensions of the molecule,[64] the moment of the N—H link is found to be 1·3D, and the value being assumed to be the same in hydrazine, the moment of the latter is calculated as 1·70D, on the basis of the configuration suggested; this result is in satisfactory agreement with the observed value 1·83D.

Some confirmation of the stereochemistry of certain elements in the second and third groups of the periodic classification has been obtained from dipole-moment data. The moment of boron trichloride is zero in solvents with which it does not combine,[65] and hence this compound probably has a symmetrical planar structure, the valency angle being 120°. This conclusion is in agreement with that reached from a study of the diffraction of electrons by boron trichloride.[66] Aluminium bromide has a very small dipole moment in carbon disulphide solution,[65, 67] but as it consists largely of double molecules in this solvent,[68] its structure is probably represented by  although there is no means of deciding between planar and tetrahedral configurations. The moments of beryllium chloride and bromide in benzene [65] are stated to be zero : if this is so, then in the bicovalent state the molecules are linear. From observations with diethylmercury and diphenylmercury,[69] it appears that these substances have small but probably definite moments ; it is suggested that the compounds have a linear structure, but that flexibility of the bonds leads to the setting up of a resultant moment. Some confirmation of this view is said to be obtained from the molecular dimensions of dibromodiphenylmercury, calculated from electron-diffraction measurements ; [70] the results are believed to be compatible with a swing of 30° of the $—C_6H_4Br$ groups on either side of a straight line through the mercury atom. The whole subject appears to be worthy of further investigation.

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[61] E. P. Linton and O. Maass, *Canadian J. Res.*, 1932, **7**, 81; *A.*, 1933, 8.

[62] W. Theilacker, *Z. physikal. Chem.*, 1933, [*B*], **20**, 142; *A.*, 1933, 338; see also E. C. E. Hunter and J. R. Partington, *J.*, 1932, 2817; *A.*, 1933, 210.

[63] W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, 1934, **30**, 898; *J. Chem. Physics*, 1934, **2**, 492; *A.*, 1934, 1158.

[64] D. M. Dennison and G. E. Uhlenbeck, *Physical Rev.*, 1932, [ii], **41**, 313; *A.*, 1932, 982.

[65] H. Ulich and W. Nespital, *Z. Elektrochem.*, 1931, **37**, 559; *A.*, 1931, 1213.

[66] R. Wierl, *loc. cit.*, ref. (17).

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[67] W. Nespital, *Z. physikal. Chem.*, 1932, [*B*], **16**, 153; *A.*, 1932, 447.

[68] H. Ulich, *ibid.*, Bodenstein Festband, 1931, 423; *A.*, 1931, 1229.

[69] E. Bergmann and W. Schütz, *ibid.*, 1932, [*B*], **19**, 401; *A.*, 1933, 210; G. C. Hampson, *Trans. Faraday Soc.*, 1934, **30**, 877; *A.*, 1934, 1157; W. J. Curran and H. H. Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 2162.

[70] H. de Laszlo, *Trans. Faraday Soc.*, 1934, **30**, 884.

INORGANIC CHEMISTRY.

1. THE PERIODIC TABLE.

IN the Mendeléef Centenary Lecture delivered before the Chemical Society by Lord Rutherford [1] a striking tribute was paid to the genius of Dimitri Ivanovitch Mendeléef, who was born on February 7th, 1834. It was very fitting that the lecturer himself should have been intimately associated with those outstanding developments which have given a new meaning to Mendeléef's famous law of the elements.

Since the Periodic Law was first enunciated, the periodicity of the elements has been fully confirmed, and although new discoveries have from time to time demanded modification of the original statement of the law, yet the fundamental ideas still remain essentially as Mendeléef set them forth. It is well known that interest in Mendeléef's generalisation was not fully aroused until the discovery of gallium in 1875 and scandium in 1879. The fact that these elements possessed the properties predicted by Mendeléef for eka-aluminium and eka-boron was very impressive, and further discoveries of new elements made it clearer still that the Periodic Law was a fundamental truth. Some twelve years ago six elements out of the possible ninety-two in the Periodic Table were still unknown. Bohr's theory of atomic structure led in 1923 to the isolation from zirconium minerals of element 72, which was named hafnium, after Hafnia, the ancient name of Copenhagen.[2] In 1925 the elements 43 and 75 were found and named masurium and rhenium respectively,[3] and in 1926 the discovery of the rare earth 61 was announced.[4] The last of the missing elements, 85 and 87, provisionally called eka-iodine and eka-cæsium, were stated to have been detected [5] in 1931—32. Three years ago, therefore, it seemed that the phase of chemistry dealing with the discovery of new elements had come to an end. It cannot be said, however, that in every case these more recent discoveries have met with general acceptance. In particular, a number of writers have questioned the significance of the evidence upon which the existence of elements 61, 85, and 87 is based. In this Report an attempt is made to state the evidence for and against these discoveries so that the reader may judge whether criticism is justified or not. Reference is also made in the following pages to elements 43 and 91, and some recent work on elements of atomic number higher than 92 is discussed.

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[1] *J.*, 1934, 635; *A.*, 1934, 713.

[2] *Ann. Reports*, 1923, **20**, 45.

[3] *Ibid.*, 1925, **22**, 63.

[4] *Ibid.*, 1926, **23**, 61.

[5] *Ibid.*, 1932, **29**, 300.

Since the time of Moseley's work, which showed definitely that an element should exist between neodymium (at. no. 60) and samarium (at. no. 62), numerous papers have been published dealing with element 61. In 1917 J. M. Eder[6] deduced from an examination of the arc spectrum of samarium that his material might contain traces of a new element, but when W. Prandtl and A. Grimm[7] in 1924 carried out an exhaustive fractionation of the cerium earths they failed to obtain any indication of an element 61. Two years later, however, the search for the new element appeared to have met with success, for J. A. Harris, L. F. Yntema, and B. S. Hopkins[8] announced that they had found weak optical absorption bands from a material obtained by the fractionation of large quantities of neodymium and samarium salts, and that these bands must be attributed to element 61. Further, they stated that they had obtained in the X-ray emission spectrum of their preparation a weak but perceptible line which they claimed was the L_a line of element 61. The mean value for this line agreed within 0·0004 Å. with the value calculated from Siegbahn's precision values, although the differences ranged from + 0·0026 to − 0·0047 Å. It was held, therefore, that element 61 had been discovered, and the name "illinium" was proposed for it. Shortly afterwards, L. Rolla and L. Fernandes[9] claimed priority of discovery, as they maintained that they had observed the absorption bands, ascribed to element 61, before Hopkins and his collaborators. R. J. Meyer[10] and R. Glocker[11] and their respective co-workers also believed that they had detected element 61 in the difficultly soluble bromate fractions of rare earths, and proved its presence by three lines in the K series of X-ray lines. At this period one gains the impression that several groups of investigators had simultaneously discovered the missing element. J. M. Cork, C. James, and H. C. Fogg[12] even stated that they had produced a sample of material containing 1% of the new element which gave seven lines of the L series of illinium. These findings, however, did not pass without criticism.

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[6] *Sitzungsber. Akad. Wiss. Wien*, 1917, IIa, 125; *A.*, 1917, ii, 185.

[7] *Z. anorg. Chem.*, 1924, **136**, 283; *A.*, 1924, ii, 615.

[8] *J. Amer. Chem. Soc.*, 1926, **48**, 1585, 1594; *A.*, 1926, 810, 780.

[9] *Gazzetta*, 1926, **56**, 435; *A.*, 1926, 1083; *Atti R. Accad. Lincei*, 1926, [vi], **4**, 498; *A.*, 1927, 190.

[10] R. J. Meyer, G. Schumacher, and A. Kotowski, *Naturwiss.*, 1926, **14**, 771.

[11] U. Dehlinger, R. Glocker, and E. Kaupp, *ibid.*, p. 772.

[12] *Proc. Nat. Acad. Sci.*, 1926, **12**, 696; *A.*, 1927, 190.

Especially noteworthy is a paper by W. Prandtl[13] in which a detailed examination is made of the evidence upon which Hopkins and his co-workers based their discovery of element 61. Prandtl shows that the absorption bands mentioned by Hopkins as occurring with neodymium salts in dilute solutions were intensified when a small quantity of neodymium nitrate was added to a large amount of samarium nitrate. Consequently, these bands did not arise from a new element lying between neodymium and samarium. Moreover, he maintained that the X-ray investigation of the rare-earth mixture was carried out in an apparatus unsuitable for the purpose, and that the so-called L_{α_1} and L_{β_1} lines of element 61 were really due to small amounts of platinum, barium, and bromine. It is interesting that later investigators have failed to obtain any evidence for element 61. In 1931 S. Takvorian[14] reported that no lines attributable to element 61 could be observed from an examination of the rare earths from Indian monazite. (Frau) I. Noddack in 1934 in an important communication[15] recorded the results of an extensive investigation at the Physikalisch Technischen-Reichsanstalt on the problem of element 61. At the request of various workers, over a period of eight years, she and W. Noddack have examined fifteen preparations by X-ray spectroscopy for the presence of element 61. In none of these preparations was any trace of this element found. Further, 100 kg. of rare earths from various sources were worked up for fractions between neodymium and samarium without giving any indication of the required element. Again, an investigation by X-ray methods of the rare-earth fractions from the Auergesellschaft which had been obtained from very large quantities of monazite did not afford, after very exhaustive fractionation, any evidence of element 61. (Frau) I. Noddack expresses the opinion that, if one surveys the negative results from so many investigations, one must conclude that there is not sufficient evidence in the literature since 1926 to say that this element has been discovered, and it must be admitted that this conclusion is a reasonable one.

Apart, however, from the controversial question whether element 61 has ever been detected, it is interesting to speculate why this element does not occur in quantity in rare-earth mixtures. (Frau) I. Noddack suggests that its absence may be due to its instability. Samarium (at. no. 62) is radioactive, according to G. von Hevesy[16] and others, and loses an α-particle. May it not be that element 61 also is radioactive, losing a β-particle, whereby its concentration in the lithosphere may become so small that it would no longer be detectable by the methods so far employed ? Or again, may not element 61 have a marked tendency to exhibit bivalency, for both samarium (at. no. 62) and europium (at. no. 63) are bivalent in some of their compounds ? To test this theory (Frau) I. Noddack has explored the possibility that element 61 may be present in minerals containing the alkaline earths, but so far, without success.

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[13] *Z. angew. Chem.*, 1926, **39**, 897; W. Prandtl and A. Grimm, *ibid.*, p. 1333; *A.*, 1927, 9.

[14] *Compt. rend.*, 1931, **192**, 1220; *A.*, 1931, 783.

[15] *Z. angew. Chem.*, 1934, **47**, 301; *A.*, 1934, 853.

[16] G. von Hevesy and M. Pahl, *Nature*, 1932, **130**, 846; *A.*, 1933, 4.

In the search for element 85, the idea that it may result from a radioactive decomposition has not been overlooked. It is obvious that it may be produced by the loss of two α-particles from actinium (at. no. 89) or by the expulsion of a β-particle from polonium (at. no. 84), and with these ideas in mind G. von Hevesy and R. Hobbie [17] have worked up a kilogram of Katanga pitchblende. The combined process of concentration and examination by *X*-ray spectroscopy makes it possible to detect less than 10^{-9} g. of the element, but even this could not be found. It will be mentioned later that F. Allison and his colleagues claim to have found elements 85 and 87.

Numerous attempts have been made to discover the elusive element 87, and a wide range of methods has been employed in the search. P. R. Genneté [18] has prepared an excellent summary of the results obtained up to 1933. The positive results are few and include the observations made by J. Papish and E. Wainer [19] in 1931. It will be recalled that these investigators prepared from 10 kg. of samarskite, rich in uranium, a cæsium preparation which they stated showed the *X*-ray lines of element 87. They heated the mineral to 1000° in a stream of hydrogen chloride, collected the sublimate, and converted it into sulphates, which were purified and fractionally crystallised as alums. The least soluble fractions were examined in a Siegbahn apparatus of high dispersion. As an example of the results obtained, the L_{β_1} line for element 87 calculated to be 0·8524 was found as 0·853 Å. L. L. Barnes and R. C. Gibbs [20] then examined by positive-ray methods a cæsium alum prepared from the samarskite used by Papish and Wainer. They obtained a result which confirmed the existence of element 87, but the intensity of the important lines was very feeble. So far, no other investigator has been able to obtain similar results. (Frau) I. and W. Noddack,[15] using various cæsium-containing minerals, have failed to isolate any preparation that gives the *X*-ray lines required for element 87, and K. T. Bainbridge,[21] employing a Dempster spectrograph, has examined cæsium chloride, made from pollucite and from lepidolite mica, with negative results. Element 87 has also been looked for as a secondary product from the disintegration of radioactive substances, but again without success. Theoretically, it may arise from element 89 (mesothorium-II) by loss of an α-particle, or from element 86 (radon) by emission of a β-ray. Experiments by G. von Hevesy [22] and O. Hahn and O. Erbacher [23] to test these possibilities have yielded negative results. The only other positive result comes from the use of a magneto-optic method, which is based on the researches of J. W. Beams and F. Allison on the Faraday effect.[24] This effect is the well-known phenomenon that the plane of polarisation of light is rotated by a liquid when this is placed in a magnetic field. It has generally been assumed that the Faraday effect does not lag behind the application of the magnetic field. J. W. Beams and F. Allison maintain, on the contrary, that there is a retardation, and their conclusions are based on this assumption. They have utilised their method for the detection of cations in analytical chemistry and also claim [25] to have found evidence of elements 85 and 87 in minerals such as lepidolite and pollucite. P. R. Genneté,[18] in a critical examination of the value of this method, concludes that the results of Allison and his collaborators must be accepted with the greatest reserve. It is not without interest to find that last year J. Papish and A. C. Shuman [26] tested the apparatus used by Allison and reported unfavourably on it. Finally, it may be mentioned that (Frau) I. Noddack [15] expresses the opinion that the results obtained by the magneto-optic method are definitely speculative and considers that the discovery of element 87 by Papish is not yet substantiated. It must be concluded that the evidence for the discovery of elements 85 and 87 is not very substantial, and that elements 61, 85, and 87 still afford ample scope for the investigator.

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[17] *Z. anorg. Chem.*, 1932, **208**, 107; *A.*, 1932, 1073.

[18] *Bull. Soc. chim.*, 1933, [iv], **53**, 140.

[19] *J. Amer. Chem. Soc.*, 1931, **53**, 3818; *A.*, 1931, 1348.

[20] *Physical Rev.*, 1932, [ii], **40**, 318; *A.*, 1933, 1223.

No account of the Periodic Table would be complete without some reference to element 43, named masurium. Although masurium was discovered at the same time as rhenium, there is a remarkable difference in their subsequent history. Very little is known even now about masurium, but the chemistry of rhenium is considerable and rapidly developing. W. Noddack, (Frl.) I. Tacke, and O. Berg[27] estimated that the lithosphere contained 10^{-13} of masurium and 10^{-12} of rhenium compared with 7×10^{-12} of manganese and 10^{-2} of iron. Their later revised estimate suggested that the two elements masurium and rhenium were present in equal amounts as 10^{-9}. This assumption makes it still more extraordinary that so little progress has been made with the study of masurium. The German investigators detected masurium by X-ray spectroscopic analysis in platinum ores, columbite, sperrylith, gadolinite, and fergusonite, and later[28] in tantalite and possibly in chrome iron ore, olivine, and pitchblende. They examined 1800 minerals and 21 meteorites for the elements 43 and 75. The evidence for the discovery depends on the identification of the K_{α_1}, K_{α_2}, and K_{β_1} lines in the X-ray spectra. The wave-lengths found were 0·672, 0·675, 0·601, and the calculated values were 0·6734, 0·6779, and 0·600 Å. respectively. Although the observed values are not identical with the calculated, they may be regarded as strong evidence of the presence of masurium, since there are no other elements which could give these results. The most successful attempt to obtain masurium has been made by W. and (Frau) I. Noddack,[29] who isolated a sulphide product containing 0·2—1% of masurium during an investigation of columbite. Although this was insufficient for an examination of the chemical properties of masurium, it served for the identification of the optical arc and spark spectral lines. Certain observers have had evidence of the presence of masurium in rhenium concentrates. For example, J. Heyrovský and V. Dolejšek[30] stated that, in their polarographic studies of manganese salt solutions with the dropping-mercury cathode, they noted a wave at − 1·15 volts in the deposition–potential curves, which they ascribed to masurium. There seems no reason to doubt the existence of element 43. J. G. F. Druce[31] has made the interesting suggestion that some rhenium preparations may be contaminated with masurium, and that this may account for some of the discrepancies in the observations and deductions of different investigators.

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[21] *Physical Rev.*, 1929, [ii], **34**, 752; *A.*, 1929, 1210.

[22] *Ann. Reports*, 1928, **25**, 317.

[23] *Physikal. Z.*, 1926, **27**, 531; *A.*, 1926, 990.

[24] *Phil. Mag.*, 1927, [vii], **3**, 1199; *A.*, 1927, 610.

[25] *Ann. Reports*, 1932, **29**, 300.

[26] *Science*, 1934, **79**, 297; *A.*, 1934, 625.

The important additions to our knowledge of protoactinium which have been made in recent years are the justification for this special reference to element 91. It will be recalled that this element

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[27] *Naturwiss.*, 1925, **13**, 567; *Sitzungsber. preuss. Akad. Wiss. Berlin*, 1925, 400; *A.*, 1925, ii, 939.

[28] *Z. angew. Chem.*, 1925, **38**, 1157; *A.*, 1926, 112.

[29] *Metallbörse*, 1926, **16**, 2129.

[30] *Chem. Listy*, 1926, **20**, 4; *A.*, 1926, 258; *Rec. trav. chim.*, 1927, **46**, 248; *A.*, 1927, 636.

[31] *Science Progress*, 1933, **27**, 687.

—the eka-tantalum of Mendeléef—was discovered independently and almost simultaneously by O. Hahn and L. Meitner in 1917 and by F. Soddy and J. A. Cranston in 1918. Not until 1927, however, was the element available in a weighable amount. In that year A. von Grosse,[32] in the Kaiser Wilhelm Institut für Chemie, isolated 2 mg. of pure Pa_2O_5, and in 1928,[33] carrying out a large-scale preparation, he obtained 9 mg. of pure oxide. As protoactinium has a half-value period of about 22,000 years, it is obvious that the element should be available in much larger quantity if sufficient starting material is used. In 1934 G. Graue and H. Käding,[34] working in O. Hahn's laboratory, reported that by working up 5·5 tons of Joachimsthal radium residues they had prepared pure K_2PaF_7 containing 0·5 g. of the element, and A. von Grosse and M. S. Agruss,[35] at the same period, described their process whereby they had obtained 0·1 g. of oxide. It will be realised that the development of the process for the isolation of these compounds has furnished valuable information concerning the chemical behaviour of this element. The details of the method of extraction used by these investigators have been published, but a working description for the preparation of pure protoactinium compounds cannot be given in a few sentences. It may, however, be of some interest to outline, briefly, the principal stages in the process used by von Grosse.[36]

Natural uranium minerals contain 8 g. of protoactinium for every 10 g. of radium, and during the process for radium extraction the protoactinium accumulates in the residue, which provides a better starting material than that found in nature. This final residue, the so-called *Rückrückstande* from Joachimsthal, has the average composition: SiO_2, 60; Fe_2O_3, 22; PbO, 8; Al_2O_3, 5; MnO, 1; CaO, 0·6; MgO, 0·5%. It also contains small quantities of titanium (0·3%), zirconium (0·1%), and hafnium, together with many other elements. The average protoactinium content is 300 mg. of Pa_2O_5 per metric ton (a concentration of 1 : 3,000,000), whereas the richest pitchblendes contain only 200 mg. per ton. The plant process is carried out in three main stages. In the first stage, treatment with hot hydrochloric acid (25%) extracts from the *Rückrückstande* the iron, the more basic oxides, and most of the lead, leaving a protoactinium concentrate consisting chiefly of silica and small amounts of zirconium, titanium, and other less basic oxides. This concentrate is fused with sodium hydroxide, and the silica is converted into sodium silicate, which is extracted with water. The residue, containing most of the protoactinium, is dissolved in acid, and silica (from the insoluble silicates) is precipitated. Soluble zirconium salts and phosphoric acid are now added to this acid filtrate, and the protoactinium is precipitated together with zirconium phosphate. The precipitated silica, which contains 70% of the protoactinium, is extracted with sodium hydroxide solution (20%), the residue dissolved in hydrochloric acid, and the protoactinium precipitated from acid solution in the usual way with zirconium phosphate, ZrP_2O_7. A characteristic reaction of protoactinium is its complete coprecipitation with zirconium phosphate. This process of A. von Grosse was modified by G. Graue and H. Käding,[34] whereby important changes were made in the sequence of the operations—fusion of the *Rückrückstande* with sodium hydroxide preceded the extraction with hydrochloric acid. Graue and Käding discuss in detail the further treatment of the precipitated zirconium phosphate. It is really a complicated problem of the separation of a tantalum–zirconium–protoactinium mixture. The separation of protoactinium from the carrier substance, zirconium phosphate, is effected by crystallisation of $ZrOCl_2$ from a hydrochloric acid solution, whereby the protoactinium in the filtrate is enriched. The final purification is effected by the alternate use of the zirconium and the tantalum reactions, and ultimately the protoactinium is isolated as K_2PaF_7 which gives no *X*-ray spectrum of foreign elements. To obtain the oxide, Pa_2O_5, this complex fluoride is heated with concentrated sulphuric acid, ammonia is added to precipitate the hydroxide, and this is ignited to the oxide.

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[32] *Nature*, 1927, **120**, 621; *A.*, 1927, 1120; *Naturwiss.*, 1927, **15**, 766; *A.*, 1928, 495; *Ber.*, 1928, **61**, [*B*], 233; *A.*, 1928, 259.

[33] See O. Hahn, *Ber.*, 1935, **68**, [*B*], 478; *A.*, 593.

[34] *Angew. Chem.*, 1934, **47**, 650; *A.*, 1934, 1186.

[35] *J. Amer. Chem. Soc.*, 1934, **56**, 2200; *A.*, 1934, 1319.

[36] *Ind. Eng. Chem.*, 1935, **27**, 422.

The element has been isolated by A. von Grosse [37] by bombarding the oxide on a copper target with a stream of electrons in a high vacuum. The use of 35,000 volt-electrons for a few hours at a current strength of 5—10 milliamps. splits the oxide into oxygen and the metal, the latter remaining as a shiny, partly sintered, metallic mass, stable to air. Another method for the preparation of the element is to decompose the halide in a high vacuum on an electrically heated tungsten filament according to the reaction :

$$2PaX_5 = 2Pa + 5X_2$$

The protoactinium forms a shiny, greyish-white, partly molten deposit on the filament. The metal does not oxidise in air, in expected contrast to metallic radium, and retains its lustre for an appreciable time. The pentachloride can be prepared readily at 550° by reaction of the oxide with carbonyl chloride :

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[37] *J. Amer. Chem. Soc.*, 1934, **56**, 2200; *A.*, 1934, 1319.

$$Pa_2O_5 + 5COCl_2 = 5CO_2 + 2PaCl_5$$

The pentachloride sublimes in transparent, nearly colourless, long needles. The chloride melts to a pale yellow liquid at 301°, but sublimes appreciably below its melting point. The complex fluoride, K_2PaF_7, crystallises in colourless long needles, very sparingly soluble in water containing hydrofluoric acid (0·5%). They are stable in air and can be dried to constant weight at 20° or 100°.

A survey of the analytical reactions of protoactinium proves definitely that the oxide Pa_2O_5 is basic, in contrast to the pentoxides of tantalum, niobium, and vanadium, which are acidic or amphoteric. This is illustrated by the fact that when a zirconium–protoactinium mixture containing tantalum is fused with potassium carbonate, the tantalum goes, at least partially, into solution, whilst the protoactinium remains in the residue. Protoactinium is evidently less basic than zirconium, for when an acid solution of zirconium chloride containing a low proportion of protoactinium reacted with an ice-cold solution of ammonium carbonate, some 12% of the zirconium but only 0·8% of protoactinium dissolved.

The importance of this work on protoactinium is not restricted to the fact that it extends in a most interesting way our knowledge of the chemistry of the elements of Group V. It also gives us new knowledge about the element which is the direct mother-substance of actinium, and enables us, for the first time, to determine this important atomic weight. The simplest and most accurate way of obtaining this atomic weight would be by a mass-spectrograph analysis. In view of F. W. Aston's success with the fluorides of uranium, tantalum, and niobium, the fluoride PaF_5 would no doubt be very suitable for the purpose, but unfortunately its preparation is excluded by the relatively large quantity of starting material required. However, using the chemical method, whereby the ratio $K_2PaF_7 : Pa_2O_5$ was determined, A. von Grosse[38] has found that the atomic weight is of the order 230·6, with an accuracy of ± 0·5 unit. This value is in complete agreement with F. W. Aston's results[39] on actinium-lead (Ac-*D* = 207) obtained by the mass spectrograph. For the chemist, this atomic-weight determination has a peculiar interest, as it adds a fourth to the three well-known anomalies of atomic weights, cobalt–nickel, argon–potassium, tellurium–iodine. Thorium (at. no. 90), which precedes protoactinium, has an atomic weight of 232·1.

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[38] *Proc. Roy. Soc.*, 1935, [*A*], **150**, 363.

[39] *Ibid.*, 1933, [*A*], **140**, 535; *A.*, 1933, 762.

A careful study of the Periodic Table must raise the pertinent question why the system of elements should end so abruptly at uranium. It is most remarkable that this element, which is considered to have the highest possible atomic number, should have an exceedingly long life, although radioactive, and should be by no means rare. It was, therefore, with unusual interest that in 1934 the announcement was received from Rome that E. Fermi,[40] investigating the products of neutron activation of various elements, had reported the possibility that an element of atomic number exceeding that of uranium had been obtained. In a later communication,[41] Fermi expresses the opinion that further experiments made by himself and his collaborators support the hypothesis that the 13-minute and 100-minute induced activities of uranium are due to transuranic elements. He states that the simplest interpretation consistent with the known facts is to assume that the 15-second, 13-minute, and 100-minute activities are chain products, probably with atomic number 92, 93, and 94 respectively and atomic weight 239. Fermi's interpretation has been subjected to criticism by various writers,[42,43] but it must be emphasised that the work of Fermi and his school is carried out with great care and considerable ingenuity, and that the conclusions which they draw are tested, wherever possible, by a variety of chemical and physical experiments. The reader will naturally enquire at this stage whether elements of atomic number greater than 92 have ever been definitely identified. The answer must be that, although there are indications that such elements may be formed by neutron activition of uranium, yet the principal workers in this field are careful to emphasise the difficulty of obtaining conclusive proof.

About the same time as Fermi's announcement in 1934, O. Koblic [44] stated that he had obtained in considerable quantity from Joachimsthal pitchblende a pure silver salt, $AgXO_4$, where X was element 93. He described the properties of the element and its compounds, estimated its atomic weight as 240 from an analysis of this silver salt, and suggested the name "bohemium" for the new element. Certain of the compounds were then submitted to (Frau) I. Noddack [43] for report. A chemical and *X*-ray investigation of the supposed silver and thallium salts RXO_4 revealed that element 93 was entirely absent, and that these substances were mixed salts of silver or thallium vanadate and tungstate with excess of tungstic acid. This claim to the discovery of element 93 has consequently been withdrawn.

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[40] *Nature*, 1934, **133**, 898; *A.*, 1934, 826. E. Fermi, E. Amaldi, O. d'Agostino, F. Rasetti, and E. Segré, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 483; *A.*, 1934, 1284.

[41] E. Amaldi, O. d'Agostino, E. Fermi, B. Pontecorvo, F. Rasetti, and E. Segré, *ibid.*, 1935, [*A*], **149**, 522; *A.*, 1935, 910.

[42] A. von Grosse and M. S. Agruss, *Nature*, 1934, **134**, 773; *A.*, 7; *Physical Rev.*, 1934, **46**, 241; *J. Amer. Chem. Soc.*, 1935, **57**, 438; *A.*, 559.

[43] *Angew. Chem.*, 1934, **47**, 653.

[44] *Nature*, 1934, **134**, 55.

S. R. C.
W. W.

2. SOME ELEMENTS AND COMPOUNDS.

Despite the ever-increasing mass of published work, it is not always realised that our knowledge of some of the most familiar inorganic substances is far from complete, and that there still remains much to discover about some of the best-known elements and compounds. It is only recently, by the use of refined physical methods, that an insight has been obtained into the detailed structure of sulphur and phosphorus, and that the constitution of bleaching powder has been elucidated. Again, during the past few years, important extensions have been made to the fundamental chemistry of common elements such as nitrogen and sulphur, for, by the utilisation of improved appliances and new experimental technique, a number of simple derivatives of great theoretical interest have been isolated. Finally, the application of modern theoretical ideas to the problems of valency and chemical combination has resulted in striking developments in the field of molecular structures. In this section of the Report an attempt is made to deal with specific examples of advances in these various directions.

It is well known that below 96° sulphur is stable in the orthorhombic form, and the chemical evidence strongly suggests the existence of an S_8 molecule in rhombic sulphur. An *X*-ray investigation [1] has shown that the structure of rhombic sulphur is definitely molecular. The S_8 molecule is a puckered 8-atom ring which may be considered as made up of two squares, one turned 45° with respect to the other (Fig. 1). The planes of the two squares are separated by 1·15 Å., the S–S distance is 2·12 Å., and the bond angle is 105°. The closest distance of approach of atoms in neighbouring molecules is about 3·3 Å. A study of the high-temperature forms of sulphur has also been made by J. J. Trillat and K. H. Meyer. It is common knowledge that when sulphur is heated to 170° it becomes highly viscous and if cooled, say, by being plunged into water, an amorphous plastic product results. If threads of this amorphous product are stretched, they show double refraction, and J. J. Trillat and H. Forestier [2] have found that they give a fibre-diagram. K. H. Meyer and Y. Go[3] deduce from an examination of this diagram that the sulphur atoms are arranged in long chains linked by covalencies arranged parallel to the direction of stretching (Fig. 2). The relationship between rhombic and elastic sulphur which these results disclose is most interesting, but the detailed mechanism whereby rhombic sulphur is converted into elastic sulphur is still under discussion.

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[1] B. E. Warren and J. T. Burwell, *J. Chem. Physics*, 1935, **3**, 6; *A.*, 285.

[2] *Bull. Soc. chim.*, 1932, [iv], **51**, 248; *A.*, 1932, **452**.

An important potential source of sulphur is the sulphur dioxide liberated in the course of many industrial processes. During the roasting of zinc, copper, lead, and nickel ores, for example, very large amounts of sulphur are lost in the form of the dioxide. The problem of obtaining sulphur from such waste gases has been under consideration at Billingham, and, as a result, a valuable process has been evolved, which M. P. Applebey has described in a recent paper.[4] Researches, extending over some years in the laboratories of Imperial Chemical Industries Ltd., have solved the difficulty of concentrating sulphur dioxide from metallurgical gases, containing 3—7% SO_2, by the ingenious method of using a sulphite–bisulphite buffer system which can be regulated to have a moderately high p_H in the cold and a much lower one when hot. This is achieved by the addition of a substance such as an aluminium salt, the hydrolysis of which is much increased by rise of temperature. It has been further demonstrated that the almost pure sulphur dioxide so obtained may be nearly quantitatively reduced by coke in accordance with the equation:

FIG. 1.

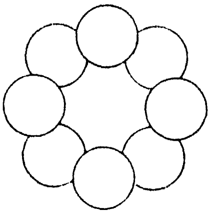
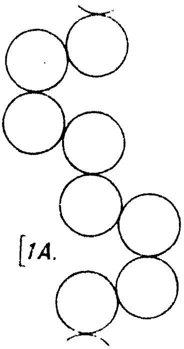


FIG. 2.



$$SO_2 + C = CO_2 + S$$

This reaction, which has been known for a long time, though generally overlooked by the text-books, furnishes a striking example of sulphur dioxide as an oxidising agent. The reduction, which takes place very rapidly and almost completely at 1100°, is exothermic, so no external energy has to be supplied when the requisite temperature has been attained. M. P. Applebey deals with the far-reaching possibilities that arise from this successful process, and the impression is gained that these developments are probably the most important which have been made in the heavy chemical industries for some considerable time.

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[3] *Helv. Chim. Acta*, 1934, **17**, 1081; *A.*, 1934, 1296.

[4] *Chem. and Ind.*, **1934**, **53**, **1097**.

The reaction between sulphur dioxide and oxygen in aqueous solution, with or without the presence of alkali, has recently become of practical importance in relation to the problem of removing sulphur dioxide from the flue gases of power stations. A review of previous work showed that the mechanism of the reaction was obscure, especially with regard to the possible effect of surfaces. In an important series of papers, R. C. Hoather and C. F. Goodeve [5] have recorded the results they have obtained from a detailed investigation of this subject.

The formation of dithionate by the oxidation of sulphurous acid and sulphites is dealt with in a comprehensive study by H. Bassett and A. J. Henry.[6] They find that oxidation of sulphurous acid and of sulphites by chlorine, iodine, and hydrogen peroxide yields but very small amounts of dithionic acid, and this is realised only under acid conditions. Oxygen gives dithionate in amounts which may be large. The yield depends on the sulphite concentration and the acidity. During the photochemical decomposition of sulphurous acid into sulphuric acid and sulphur, no dithionate appears to be formed. The theoretical considerations involved in the different reactions are carefully discussed.

In a previous Report an account was given of the preparation of sulphur monoxide by an electric discharge in a mixture of sulphur dioxide and sulphur vapour at low pressures. P. W. Schenk [7] has now shown that it is possible to obtain a gas containing 40% of sulphur monoxide, mixed with the dioxide, by the direct combustion of sulphur. K. Heumann [8] in 1883 had observed that sulphur at 200° was slowly oxidised, with a feeble phosphorescence, and that a peculiar smell was noticed which he ascribed to sulphur monoxide. He tried unsuccessfully to prove the existence of the monoxide by leading the gas into alkali. Schenk [7] now finds that oxidation of sulphur with air at atmospheric pressure gives only a small concentration of monoxide when determined spectroscopically, but, by operating at low pressures with oxygen, concentrations up to 40% of monoxide may be obtained when the optimum temperature for the reaction has been realised. This optimum temperature must be determined experimentally. At pressures of 30, 8, and 5 mm., the yields of sulphur monoxide have been found to be 7, 30, and 40% respectively. Pressures of oxygen lower than 5 mm. cannot be used, as the sulphur flame is extinguished. In a recent communication C. W. Montgomery and L. S. Kassel[9] calculate the equilibrium constants for the following reactions from spectroscopic data:

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[5] *Trans. Faraday Soc.*, 1934, **30**, 626, 630, 1149, 1156; *A.*, 1934, 1086, 1157; *A.*, 1935, 42.

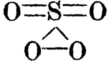
[6] *J.*, 1935, 914; *A.*, 1090.

[7] *Z. anorg. Chem.*, 1934, **220**, 268; *A.*, 1935, 51.

[8] *Ber.*, 1883, **16**, 139.

$$(a)\ 2SO = S_2 + O_2,\ (b)\ 2SO = SO_2 + \tfrac{1}{2}S_2$$

They find that, at very low temperatures, the equilibrium lies right over on the left in reaction (*a*). In reaction (*b*) they report that an appreciable vapour pressure of sulphur monoxide only comes into equilibrium with the dioxide and sulphur at about 2000° Abs. These findings are in agreement with the qualitative observations made by Schenk. As the temperature of the sulphur flame is so low, an equilibrium position in the sense of the reaction (*b*) is not attained. It follows, therefore, that the sulphur monoxide formed in (*a*) is removed from the sphere of reaction before the equilibrium required by (*b*) is operating. Schenk[10] has studied, by density determinations, the decomposition which sulphur monoxide undergoes into sulphur and sulphur dioxide. His results show, from the pressure changes observed, that when sulphur monoxide is decomposed according to reaction (*b*), 64% of the sulphur monoxide molecules are associated to $(SO)_2$.

Although the existence of a tetroxide of sulphur has been suspected by various investigators, it has only recently been isolated. R. Schwarz and H. Achenbach[11] have now prepared it by the action of the glow discharge on a mixture of sulphur dioxide and oxygen (in the proportion 1 : 10) at 0·5 mm. pressure. The reaction products are passed through two vessels cooled in liquid air, a white solid being obtained. This is freed from sulphur dioxide and ozone by warming to − 30° in a current of oxygen, the tetroxide then remaining. The yield from an experiment lasting six hours is 0·1 g. Sulphur tetroxide is a white solid which begins to decompose at − 5° with evolution of oxygen, and at 3° it melts with decomposition, giving oily drops of S_2O_7. By the freezing-point method a molecular-weight determination in pure sulphuric acid gave a value 95 in close agreement with 96 required by the simple formula SO_4. Schwarz and Achenbach suggest the structural formula  $O{=}S{=}O$, $O{-}O$ for the oxide. Although theoretically this tetroxide could be the anhydride of permonosulphuric acid, there is no evidence that it will undergo hydration to H_2SO_5. When the tetroxide is dissolved in dilute sulphuric acid at 0°, slow decomposition takes place with oxygen evolution, but no H_2SO_5 appears to be formed. This inability to become hydrated is attributed by Schwarz and Achenbach to the co-ordinative saturated character of the sulphur. Sulphur tetroxide is an excellent oxidising agent: it will oxidise aniline to nitrobenzene, and bivalent manganese to the septavalent state.

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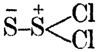
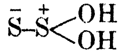
[9] *J. Chem. Physics*, 1934, **2**, 417; *A.*, 1934, 966.

[10] P. W. Schenk and H. Platz, *Z. anorg. Chem.*, 1935, **222**, 177; *A.*, 593.

[11] *Ibid.*, 1934, **219**, 271; *A.*, 1934, 1183.

A. H. Spong[12] has concluded that ordinary sulphur monochloride is probably a mixture of the two forms (1)  $\overset{-}{S}{-}\overset{+}{S}{<}^{Cl}_{Cl}$ and (2) Cl·S·S·Cl. G. Giacomello[13] has now studied the reaction of phenol and of β-naphthol with sulphur monochloride in benzene. From the reaction with phenol he isolated one compound with the probable structure PhO·S·S·OPh, and from the β-naphthol reaction the derivative $C_{10}H_7{\cdot}O{\cdot}S{\cdot}O{\cdot}C_{10}H_7$. On the other hand, from *p*-chlorophenol he obtained two products $C_6H_4Cl{\cdot}O{\cdot}S{\cdot}S{\cdot}O{\cdot}C_6H_4Cl$ and $C_6H_4Cl{\cdot}O{\cdot}S{\cdot}O{\cdot}C_6H_4Cl$. These results are entirely in agreement with the view that sulphur monochloride is a mixture of (1) and (2), and if this view is correct, then the hypothetical thiosulphurous acid should exist in two isomeric forms (1)  $\overset{-}{S}{-}\overset{+}{S}{<}^{OH}_{OH}$ and (2) HO·S·S·OH. F. Lengfeld[14] some 40 years ago examined the action of alcohol-free sodium methoxide or ethoxide on a well-cooled solution of sulphur monochloride in light petroleum. He obtained one ester, in each case as a colourless oil. A. Meuwsen[15] now claims that two isomeric esters can be isolated, one similar to the colourless oil of Lengfeld, and the other a greenish-yellow oil of different constitution but of the same molecular weight. The colourless oil he considers to have the constitution OR·S·S·OR whereas to the other ester he assigns the formula $S{=}S(OR)_2$. H. Stamm[16] maintains, however, that Meuwsen's greenish-yellow ester is merely Lengfeld's colourless ester contaminated with about 2·5% of sulphur monochloride, and this would account for the chemical and physical differences which have been noted.

R. Scholder and G. Denk[17] have prepared the first salt of the hypothetical sulphoxylic acid, H_2SO_2. When aqueous solutions of cobaltous chloride and sodium hyposulphite ($Na_2S_2O_4$) reacted in the presence of ammonia, ethylenediamine, or pyridine, a dark red solution was formed which, on dilution with water, gave a dark brown flocculent precipitate of cobalt sulphoxylate, $CoSO_2,xH_2O$, probably in a polymerised form.

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[12] *J.*, 1934, 485; *A.*, 1934, 605.

[13] *Atti R. Accad. Lincei*, 1935, [vi], **21**, 36; *A.*, 614.

[14] *Ber.*, 1895, **28**, 449.

[15] *Ber.*, 1935, **68**, [*B*], 121; *A.*, 326.

[16] *Ibid.*, p. 673; *A.*, 729.

[17] *Z. anorg. Chem.*, 1935, **222**, 17; *A.*, 461.

A. M. Middleton and A. M. Ward[18] have investigated the composition and properties of precipitated nickel and cobalt sulphides. They find that, with air exclusion, the sulphides formed are $Ni(SH)_2$, $Co(SH)_2$, and $Co(SH)_3$, which yield NiS, CoS, and Co_2S_3 when dried in nitrogen. In the presence of oxygen, however, variable addition takes place, initially at the sulphur atoms in accordance with the scheme $\mathrm{Ni}\left(\mathrm{S}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{H}\end{smallmatrix}\right)_2$, $\mathrm{Co}\left(\mathrm{S}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{H}\end{smallmatrix}\right)_3$. This is accompanied by intramolecular rearrangement. Drying of the oxygenated sulphides results in a partial elimination of hydrogen sulphide and water, and further oxygenation may proceed. The dried and the undried oxygenated sulphides are the substances usually obtained in qualitative analytical procedure.

Although a peroxide of nitrogen appears to be formed by the action of a silent discharge on a mixture of oxygen and nitrogen dioxide,* its existence has hitherto only been indicated by a change in colour of the mixture and the appearance of certain characteristic spectral lines. Now, however, R. Schwarz and H. Achenbach[19] have succeeded in preparing pure nitrogen trioxide, NO_3, and examining its properties. The apparatus they employed was essentially the same as that used by them for their successful synthesis of sulphur tetroxide. A mixture of nitrogen dioxide and oxygen in the proportion 1 : 20 at a pressure of 1 mm. was passed through the apparatus and submitted to a glow discharge. The $NO_2 : O$ ratio must be carefully adjusted. Lower oxides of nitrogen are formed unless a large excess of oxygen is present, but too great an excess gives ozone. The reaction products were condensed in vessels cooled with liquid air, and a pale blue condensate was obtained, apparently a mixture of dinitrogen trioxide and higher oxides. By modifying this apparatus so that the condensing tube formed part of the discharge tube, they obtained a colourless deposit of pure nitrogen trioxide, NO_3. It is stable at $-142°$, above which it slowly decomposes into nitrogen dioxide and oxygen. In aqueous media it is relatively stable. For example, at 15—20°, the oxidation

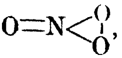
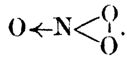
[18] *J.*, 1935, 1459.

[19] *Ber.*, 1935, **68**, [*B*], 343; *A.*, 457.

* The nomenclature used in this article denotes the actual numbers of atoms of nitrogen and oxygen in the molecule; *e.g.*, dinitrogen trioxide N_2O_3, nitrogen trioxide NO_3.—Ed.

value of nitrogen trioxide in sulphuric acid (*N*/5) requires about 50 hours to sink to zero. Again, when the trioxide is dissolved in nitric acid (2*N*) and potassium iodide is added, although iodine is liberated immediately, the reaction reaches completion only after 30 minutes. With sodium hydroxide the trioxide reacts thus :

$$2NO_3 + 2NaOH = NaNO_3 + NaNO_2 + O_2 + H_2O$$

The reaction takes place in two stages. In the presence of water, the trioxide is decomposed into the dioxide and oxygen and the dioxide then yields NO_2' and NO_3'. The trioxide does not function, therefore, as an acid anhydride. Although direct determinations of molecular weight are impossible owing to the instability of the compound, the authors consider that it has the monomeric form. They base this opinion on the very low temperature of condensation of the trioxide and its spectroscopic behaviour. Further, they consider that it must have a co-ordinatively unsaturated character from the fact that it can be extracted from aqueous media by ether. The distribution coefficient between water and ether is, in fact, 1 : 3. As hydrolysis in water is not accompanied by the production of hydrogen peroxide, the constitution $NO_2–O–O–NO_2$ is excluded and identity with the dimeric oxide N_2O_6 not possible. The authors believe, therefore, that their new trioxide has the formula  $\mathrm{O{=}N}\Big\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}$, which would be more correctly written as  $\mathrm{O{\leftarrow}N}\Big\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}$.

T. M. Lowry and J. T. Lemon [20] report that when dry dinitrogen pentoxide (N_2O_5) is vaporised in a stream of ozonised oxygen and then passed through a glass tube heated by a small flame, the colourless gas becomes brown, through the formation of nitrogen dioxide, a short distance before the flame is reached. A narrow zone of a dark grey-blue colour is, however, seen hovering at the boundary, and this is preceded by a zone of clear blue. In a long tube the blue flame thus formed " strikes back " from time to time at the rate of about 10 cm. per second to the point at which the gas enters the tube, which is then filled from end to end with brown nitrogen dioxide. When the concentration of dinitrogen pentoxide is low, the grey boundary between the colourless incoming gas and its pale brown decomposition products remains stationary and does not strike back. It is suggested that the formation and disappearance of the blue zone may be due to the production and decomposition of a higher oxide of nitrogen; *e.g.*, $N_2O_5 + O_3 = 2NO_3(\text{blue}) + O_2$; $2NO_3 = 2NO_2 + O_2$. The temperature at the boundary is probably below 100°. In a study of the binary system N_2O_4–N_2O_5 Lowry and Lemon [21] find that dinitrogen tetroxide

[20] *Nature*, 1935, **135**, 433; *A.*, 593.

[21] *J.*, 1935, 692; *A.*, 824.

and pentoxide give a simple freezing-point diagram with a eutectic at 10·8% N_2O_5 and − 15·8°.

During recent years some exceptionally interesting compounds have been isolated from reactions involving fluorine. G. H. Cady[22] has now investigated the action of fluorine on nitric acid (3*N*) and thereby discovered the new gaseous compound, NO_3F. In his experiments, Cady sometimes experienced explosions, but O. Ruff and W. Knasnik[23] find that the danger of explosion is minimised by the use of nitric acid of higher concentration, and that it disappears entirely if pure nitric acid (100%) is employed. At low temperatures, *e.g.*, − 35°, the reaction is incomplete, but at + 20° it proceeds quantitatively in accordance with the equation

$$HNO_3 + F_2 = NO_3F + HF$$

The apparatus used is constructed partly of quartz glass and partly of ordinary glass. The hydrogen fluoride liberated in the reaction is absorbed by anhydrous potassium fluoride, and the other products are condensed in receivers cooled with liquid air. The condensate is fractionally distilled at 100 mm. pressure through a quartz-glass column, and the portion passing over at − 79°/99 mm. is pure NO_3F. Other fractions consist of SiF_4, H_2SiF_6, and H_2F_2. A molecular-weight determination by the density method gave the theoretical value for the molecule NO_3F. The fluoride, which is normally a gas with critical temperature estimated to be 67·2°, condenses to a colourless liquid, b. p. − 45·9°/760 mm., and to a white solid, m. p. − 175°. The density of the solid at − 193·2° is 1·951, and that of the liquid is $2{\cdot}2148 - 0{\cdot}003114T$. Solid or liquid NO_3F is exploded by mechanical shock. The vapour pressure has been measured with a quartz-spiral manometer between − 128° and − 68° and is given by $\log p = -1044{\cdot}9/T + 7{\cdot}478$, and the latent heat of vaporisation is 4726 g.-cals. per mol. The gas is stable in dry glass or quartz, but with water it gives oxygen and fluorine monoxide together with nitric acid and hydrogen fluoride. It reacts with dilute sodium hydroxide solution (2%), OF_2 being liberated :

$$2NO_3F + 2NaOH = 2NaNO_3 + OF_2 + H_2O$$

If a more concentrated sodium hydroxide solution (20%) is employed, the initially formed fluorine monoxide decomposes in the usual way and oxygen alone is obtained. These experimental findings characterise NO_3F as a derivative of the fluorine monoxide, OF_2, in which a fluorine atom is replaced by the NO_2 group, *i.e.*,

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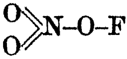
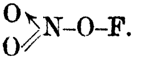
[22] *J. Amer. Chem. Soc.*, 1934, **56**, 2635; *A.*, 1935, 181.

[23] *Angew. Chem.*, 1935, **48**, 238; *A.*, 715; D. W. Yost and A. Beerbower, *J. Amer. Chem. Soc.*, 1935, **57**, 782; *A.*, 715.

 $\begin{smallmatrix}O\\O\end{smallmatrix}\!\!>\!N{-}O{-}F$, or in modern nomenclature  $\begin{smallmatrix}O\nwarrow\\O\end{smallmatrix}\!\!>\!N{-}O{-}F$. Although the reaction of NO_3F with water or sodium hydroxide solution does not give an explosion, contact with alcohol, ether, or aniline causes one immediately. On the other hand, with glycerol, acetic acid, or acetone no reaction is perceptible. Moreover, NO_3F is appreciably soluble in acetone. The odour of the new compound is described as irritating.

K. Gleu and R. Hubold[24] have reinvestigated the per-acid which is formed on mixing a nitrite solution with acidified hydrogen peroxide and to which Raschig and other investigators have given the formula HNO_4 and the name pernitric acid. Gleu and Hubold prepared the supposed pernitric acid by adding to a solution of sodium nitrite (1 mol.) and hydrogen peroxide ($>$ 1 mol.) much ice and then the equivalent amount of sulphuric acid (2*N*), excess of sodium hydroxide being added after two seconds. In the intensely yellow solution produced, 70% of the nitrite may be converted into the per-acid under the best experimental conditions. To obtain this result it is most important to observe the correct interval of time between addition of acid and of alkali. The excess of hydrogen peroxide, in the presence of sodium nitrite and the sodium salt of the per-acid, was determined by titration with sodium hypochlorite (0·1*N*) in alkaline solution in the presence of ten drops of potassium iodide (0·1*N*) until the colour of the ruthenium-red indicator was discharged. Excess of arsenious oxide (0·1*N*) was added immediately and back-titrated with sodium hypochlorite, the same indicator being used, to determine the active oxygen in the per-acid. The NO_2' was determined by reduction to ammonia with vanadyl sulphate, $VOSO_4$, and distillation into acid. Under these conditions any nitrate is unaffected. The ratio, active $O : NO_2'$, was always 1 : 1, proving the presence of pernitrite $HNO_2{\cdot}O$ and absence of pernitrate. These findings confirm the views of J. Schmidlin and P. Massini[25] put forward in 1910. It may be mentioned again that the nitrogen trioxide (NO_3) recently prepared by Schwarz and Achenbach did not prove to be the anhydride of pernitric acid.

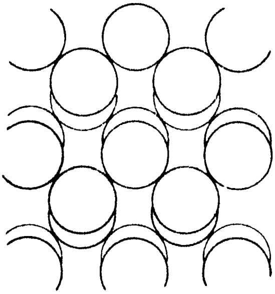
Phosphorus crystallises in a number of allotropic forms, three of which, the white, the red, and the black variety, are easily distinguished because of their widely differing physical and chemical properties. It is well known that white phosphorus is easily changed into the red variety by heat, light, or *X*-rays, but that to convert white into black phosphorus[26] a pressure of 12,000 atmo-

[24] *Z. anorg. Chem.*, 1935, **223**, 305. [25] *Ber.*, 1910, **43**, 1162; *A.*, 1910, ii, 498.

[26] P. W. Bridgman, *J. Amer. Chem. Soc.*, 1914, **36**, 1334; *A.*, 1914, ii, 647.

spheres is necessary at a temperature of 200°. Recently, black phosphorus has been made from white phosphorus by a pressure of 35,000 atmospheres at room temperature.[27] The density of black phosphorus is very high, being 2·6—2·7, as against 1·83 for white and 2·34 for red phosphorus. All three varieties when heated give a vapour composed of P_4 molecules, which condenses to white phosphorus. At lower temperatures (100° in a vacuum), however, the vapour of red phosphorus condenses unchanged, but the vapour density is so low that no molecular-weight determination has yet been made. These facts seem to indicate that white phosphorus is composed of more or less loosely-bound P_4 molecules, which readily break up to form the more stable structures of red and black phosphorus. It is most difficult to come to a decision in this matter, for data on phosphorus are confusing and incomplete, and until recently none of the crystal structures had been satisfactorily worked out by *X*-ray methods. An important advance has now been made by R. Hultgren, N. S. Gingrich, and B. E. Warren [28] as a result of their investigation of the crystal structure of black phosphorus. They find that the unit cell of black phosphorus consists of two double layers, one of which is shown in Fig. 3. Each atom is bound to three nearest neighbours at 2·18 Å. in agreement with the accepted atomic radius of 1·10 Å. and with the co-ordination to be expected from covalent bonding of phosphorus. Two of the bonds are in the plane of the layer at 99° from one another; the third is between layer halves at 103° 30′ from both, making the average bond angle 102°. This agrees with the tendency of bond angles to be nearer tetrahedral for the lighter elements of the periodic group. The decisively covalent character of phosphorus is clearly shown by the fact that the distance between bonded atoms is only 2·18 Å. compared with 3·68 Å. as the closest

FIG. 3.



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[27] P. W. Bridgman, *Physical Rev.*, 1934, **45**, 844.

[28] *J. Chem. Physics*, 1935, **3**, 351; *A.*, 919.

approach between atoms in different layers. In arsenic, which is appreciably more metallic than black phosphorus, the bonds are less sharply differentiated; the three nearest neighbours are at 2·51 Å., with three more atoms at 3·15 Å. Atomic distribution curves of crystalline and amorphous black and red phosphorus, obtained by the method of Fourier analysis, furnished a valuable clue to the structure of red phosphorus, for they showed that each atom formed three covalent bonds in the normal manner. Moreover, the fact that the second peak was at practically the same position as in black phosphorus suggests that the bond angles are nearly the same.

Ortho-salts, such as Na_3NO_4, Na_3NO_3, Na_6ZnO_4, and Na_4CuO_3, have been prepared [29] by the action of sodium oxide, Na_2O, on the salts of oxy-acids or on weakly acidic metallic oxides. They are usually decomposed by water or carbon dioxide, so cannot be prepared from alkali hydroxides or carbonates. The proof of the existence of these ortho-salts has been established by *X*-ray analysis. The preparation of Na_3NO_4 brings out an interesting relationship between nitrogen and phosphorus. However, as 4 is the maximum co-ordination number of nitrogen, it will, presumably, not be possible to prepare the nitrogen analogue of the hypothetical H_5PO_5, esters of which have been isolated.[30]

The constitution of bleaching powder has been the subject of investigation and speculation for many years. The older methods of examination, depending on such properties as solubility, vapour pressure, mode of chemical decomposition with heat or acids of the carbonic and hydrochloric type, have been used at various times but with no great measure of success. The problem has now [31] been attacked by phase-rule studies, by extended microscopic examination, and by the use of *X*-ray powder photographs. As a result of the phase-rule work, all the pure compounds which could be isolated under equilibrium conditions from the system $CaO–CaCl_2–Ca(OCl)_2–H_2O$ below 40° have been defined and used as a basis for comparison with the solid phases present in bleaching powder. It has been established that the first stage, in the reaction between chlorine gas and calcium hydroxide in the preparation of bleaching powder, is the formation of the basic hypochlorite $Ca(OCl)_2,2Ca(OH)_2$ and the basic chloride $CaCl_2,Ca(OH)_2,H_2O$. On further chlorination, the former is converted into another substance which appears to be a mixed crystal whose chief constituent is calcium hypochlorite. Ordinary bleaching powder, containing about 35% of available chlorine, is a mixture of this hypochlorite mixed crystal with the basic chloride $CaCl_2,Ca(OH)_2,H_2O$. On further chlorination, the latter is partly but never completely converted into hydrated calcium chloride (usually the tetrahydrate, $CaCl_2,4H_2O$) whilst the hypochlorite mixed crystal persists, with gradually changing properties. The most highly chlorinated sample which was examined consisted of hypochlorite mixed crystal, $CaCl_2,4H_2O$, and $CaCl_2,Ca(OH)_2,H_2O$. The non-deliquescent nature of ordinary bleaching powder and the difficulty of introducing more than 35% of available chlorine into the solid are due to the presence of the basic chloride

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[29] E. Zintl, M. Morawietz, and G. Woltersdorf, *Naturwiss.*, 1935, **23**, 197; E. Zintl and W. Haucke, *Z. physikal. Chem.*, 1935, **174**, 312; *A.*, 1936, 16.

[30] L. Anschütz and W. Broeker, *Ber.*, 1926, **59**, 2848; *A.*, 1926, 146.

[31] C. W. Bunn, L. M. Clark, and I. L. Clifford, *Proc. Roy. Soc.*, 1935, [*A*], **151**, 141; *A.*, 1214.

$$CaCl_2,Ca(OH)_2,H_2O,$$

which appears to be a very stable substance.

R. K. Bahl and J. R. Partington[32] have reinvestigated the lower oxides and sulphates of iodine. Contrary to some statements in the literature, which are reproduced in text-books, they prove that the interaction of iodine and cold concentrated nitric acid (*d*, 1·5) produces the pentoxide I_2O_5 and not the dioxide. In conformity with the weakly basic properties of iodine, they find that basic salts are more stable than the normal ones. They were unable, however, to obtain Chrétien's sulphate, $I_2O_3,SO_3,\frac{1}{2}H_2O$, by heating a mixture of iodic acid and concentrated sulphuric acid till iodine is evolved. The analysis showed that the product was probably I_2O_3,H_2SO_4 containing some I_2O_4,H_2SO_4.

Although numerous attempts have been made to prepare compounds of the rare gases, practically all investigations have served only to show the inertness of these elements. P. Villard,[33] however, in 1896 claimed to have obtained an unstable hydrate of argon, and since then hydrates[34] of krypton and xenon have been reported. Prompted by the idea that boron, in the trifluoride, BF_3, is very reactive by reason of its incomplete octet, H. S. Booth and K. S. Willson[35] have examined the system argon–boron trifluoride by thermal analysis. A graph of the freezing points against composition exhibited maxima and minima. The maxima corresponded to the ratios A,BF_3; $A,2BF_3$; $A,3BF_3$; $A,6BF_3$; $A,8BF_3$; and $A,16BF_3$, indicating compound formation, but the compounds are unstable and dissociate above their melting points. From the shape of the curve, the ratio $A,2BF_3$ appears to be the most stable.

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[32] *J.*, 1935, 1258; *A.*, 1334.

[33] *Compt. rend.*, 1896, **123**, 377; *A.*, 1897, ii, 31.

[34] R. de Forcrand, *ibid.*, 1923, **176**, 355; 1925, **181**, 15; *A.*, 1923, ii, 239; 1925, ii, 812.

[35] *J. Amer. Chem. Soc.*, 1935, **57**, 2273.

The conclusion that the association of argon with the boron fluoride is of the type $BF_3 \leftarrow A$ analogous with $BF_3 \leftarrow NH_3$ must be accepted with reserve. The function of the BF_3 may be similar to that of water in the hydrates of the inert gases. In N. V. Sidgwick's [36] opinion, the water is held by the van der Waals forces in the crystal along with those of the solute, and the simple numerical ratio of the different kinds of molecules merely reflects the geometrical regularity of the crystal.

So far, no exception has been found to the generalisation that all elements with a covalency of 6 have the six valencies arranged in the form of an octahedron. When, however, quadricovalent atoms are considered, no such simple generalisation is available. It will be recalled that in 1931 L. Pauling [37] applied wave-mechanical methods to the problem of covalent linkages and showed that for 4-covalent atoms, in which electrons from the first two sub-groups (*s* and *p*) of the outer level are used in chemical bonds, the stable configuration is tetrahedral. In the case of the transition elements, however, one or more electrons used in binding may belong to the *d* sub-group of the incomplete inner level, and in these cases, the four covalencies may be distributed in a plane. Moreover, since the *d* electrons are chiefly responsible for the magnetic moment of the atom, sharing of them should reduce this property, so that 4-covalent nickel compounds should be diamagnetic. Pauling's conclusions have been criticised by W. Heisenberg [38] and others, but appear to be essentially correct. The point to be recognised in the case of the transition elements is that the results are probably permissive, *i.e.*, they show that the metals in question may have, but not necessarily must have, a planar distribution of valencies. That this interpretation is correct is indicated by some recent work of H. M. Powell and A. F. Wells.[39] They examined the complex salt Cs_3CoCl_5 by *X*-ray analysis, and found that the group $CoCl_4$ had an approximately regular tetrahedral configuration, thereby proving that the transition element cobalt can actually be tetrahedral when 4-covalent.

To Pauling belongs the credit of first suggesting that nickel in its 4-covalent state may have a planar distribution of valencies, and it is remarkable that Werner omitted it from the list of elements which he predicted would give planar structures. Pauling's conclusion that 4-covalent nickel should be planar and diamagnetic received strong support from the isolation, by S. Sugden [40] in 1932, of two diamagnetic compounds of nickel with benzylmethylglyoxime. As a matter of historical interest, it should be mentioned that in 1910, L. A. Tschugaeff[41] discovered that nickel bis(monomethylglyoxime) could occur in two isomeric forms, but he did not suggest that a possible explanation of the isomerism lay in the planar distribution of the nickel valencies. Recently, H. J. Cavell and S. Sugden[42] have shown that the occurrence of pairs of isomerides appears to be general for the nickel derivatives of unsymmetrical glyoximes, and that the explanation must be that nickel is capable of forming 4-covalent compounds of planar type. F. P. Dwyer and D. P. Mellor[43] have recorded the preparation of two inner complex compounds of palladium with benzylmethylglyoxime, and adduced evidence to show that these substances are *cis-* and *trans-*isomerides (I and II) of bis-*anti*-benzylmethylglyoximepalladium.

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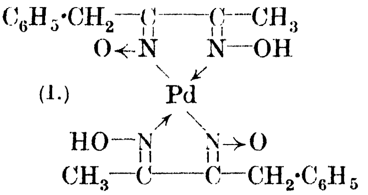
[36] "The Covalent Link in Chemistry," 1933, p. 29.

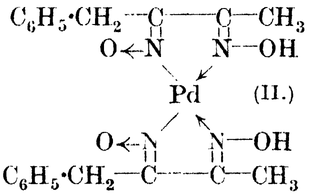
[37] *J. Amer. Chem. Soc.*, 1931, **53**, 1367; *A.*, 1931, 670.

[38] See *Ann. Reports*, 1931, **28**, 367.

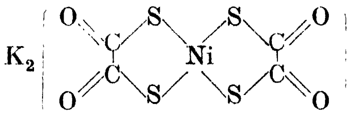
[39] *J.*, 1935, 359; *A.*, 570.

[40] *J.*, 1932, 246; *A.*, 1932, 272.


(I.)


(II.)

Further support for Pauling's predictions has been obtained from an examination of the nickel and palladium derivatives of salicylaldoxime.[44] These compounds have been shown, by *X*-ray analysis, to be isomorphous and to have a *trans*-planar structure. Moreover, the nickel compound has been found to be diamagnetic. A striking example of planar nickel in a co-ordination compound of quite a different type has been discovered in an examination of the dithio-oxalates of nickel, palladium, and platinum.[45] The anhydrous potassium nickelodithio-oxalate (III) is completely isomorphous


(III.)

with the corresponding palladium and platinum derivatives, and a detailed *X*-ray examination has shown that the valencies of the 4-covalent nickel, palladium, and platinum are in a plane with the metal atom.

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[41] *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1466; *A.*, 1911, i, 261; *Chem. Zentr.*, 1911, **82**, i, 871.

[42] *J.*, 1935, 621; *A.*, 980.

[43] *J. Amer. Chem. Soc.*, 1935, **57**, 605; *A.*, 752.

[44] E. G. Cox, F. W. Pinkard, W. Wardlaw, and K. C. Webster, *J.*, 1935, 459; *A.*, 684.

[45] E. G. Cox, W. Wardlaw, and K. C. Webster, *J.*, 1935, 1475.

In view of the fact that compounds of 4-covalent cobalt may be tetrahedral, the question naturally arises whether the 4-co-ordinated compounds of nickel, palladium, and platinum are invariably planar. If Pauling's prediction is true that 4-covalent compounds of the transition elements would be diamagnetic when the four electron-pair bonds lie in a plane, then some recent work by R. B. Janes [46] on the magnetic susceptibilities of typical palladium derivatives indicates that palladium is invariably planar. He examined a wide range of derivatives, of which the following are typical:

Group 1. Palladous salts with four other groups in the molecule: $PdCl_2,2H_2O$; $PdCl_2,2NH_3$; K_2PdCl_4; $K_2Pd(CN)_4$.

Group 2. Palladous inner complex salts: palladium dimethylglyoxime.

Group 3. Palladous salts where a double molecule is present: $[Pd(NH_3)_2Cl_2]_2$.

In every case the magnetic susceptibilities were diamagnetic. The corresponding platinum compounds have been less extensively investigated,[47] but the several salts which have been measured are all diamagnetic. This physical evidence is in entire agreement with the available *X*-ray and chemical evidence, and in view of the diverse nature of the compounds which have been studied, there appears to be no doubt that the planar configuration is quite general for 4-covalent compounds of bivalent palladium and platinum, and it can only be modified in very special cases, such as may arise with ter- and quadri-dentate groups.

The evidence from magnetic susceptibility measurements in the case of nickel, however, indicates that 4-covalent nickel is not invariably planar. Nickelous salts of the type of Group 1 (above) are paramagnetic, except $Ni(CO)_4$ and $K_2Ni(CN)_4$ which are diamagnetic. If, therefore, Pauling's reasoning is sound, then in the case of nickel only a few molecules of the type of Group 1 are planar, in contrast to the cases of palladium and platinum, where the planar configuration is always assumed. This conclusion, that the distribution of the valencies in compounds of 4-covalent nickel may be either tetrahedral or planar, is in agreement with the recent discovery that quadricovalent cupric compounds may be planar. In 1926, W. H. Mills and R. A. Gotts [48] showed that 4-covalent copper in its benzoylpyruvic acid derivative gave rise to optical activity, and so presumably belongs to the tetrahedral type. Now, E. G. Cox and K. C. Webster [49] have examined by *X*-ray analysis a range of chelated 4-covalent compounds of bivalent copper, including the copper salts of acetylacetone and benzoylacetone, and have definitely established that these substances possess a planar structure. The result is of interest from another point of view, for S. Sugden [50] has shown that a number of compounds of this type are paramagnetic. According to Pauling, a planar configuration is to be expected when *s*, *p*, and *d* electrons are involved in valency bonds. It is possible, therefore, that bivalent copper (at. no. 29) may possess a complete 3_3 sub-group of ten electrons, some being shared, instead of an incomplete sub-group as is usually supposed. This would involve one unpaired electron $\begin{matrix}1_1 & 2_1 & 2_2 & 3_1 & 3_2 & 3_3 & 4_1 \\ 2 & 2 & 6 & 2 & 6 & 10 & 1\end{matrix}$ in the fourth principal quantum level, giving rise to a paramagnetic moment of the same order as that actually observed by S. Sugden.[50]

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[46] *J. Amer. Chem. Soc.*, 1935, **57**, 471; *A.*, 573.

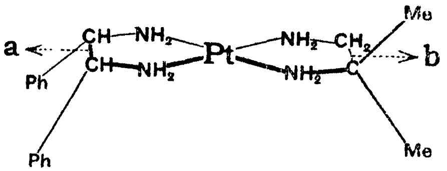
[47] D. M. Bose, *Z. Physik*, 1930, **65**, 677; *A.*, 1931, 25.

[48] *J.*, 1926, 3121; *A.*, 1927, 149.

[49] *J.*, 1935, 731; *A.*, 920.

The structure proposed by Werner for platinous compounds of the type PtA_2B_2 was that the valencies had a planar arrangement.

FIG. 4.



A test of this, and a differentiation between a planar and a tetrahedral distribution of valencies, is provided by the substitution derivatives of bisethylenediaminoplatinous salts $[Pt\,en_2]X_2$. In an important communication by W. H. Mills and T. H. H. Quibell,[51] the preparation of the diphenyl dimethyl derivatives has been described and the optical activity of the compounds (see Fig. 4) leaves no doubt that the planar arrangement proposed by Werner is the correct one. The salts investigated proved capable of resolution into antimeric optically active forms showing a high degree of optical stability. The regular tetrahedral arrangement is thereby excluded, and no reason exists for inferring a pyramidal rather than the more symmetrical planar configuration. The authors mention that the iodide and chloride crystallise with water of crystallisation, but express the opinion that there is no reason to doubt that the central platinum atom of the complex cation is truly 4-covalent. The planar arrangement of the platinum valencies with the intervalency angle of 90° is shown to give rise to a practically strainless ring, whilst an arrangement with a tetrahedral valency angle would create a very considerable strain in a five-atom ring composed of carbon and nitrogen atoms and one 4-covalent platinum atom.

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[50] *J.*, 1932, 161; *A.*, 1932, 324.

[51] *J.*, 1935, 839; *A.*, 1057.

The structure and configuration of certain diamminopalladium compounds have been studied by chemical and *X*-ray methods, and the findings are fully in agreement with Werner's view. A deep red, highly crystalline form of $Pd(NH_3)_2Cl_2$, has been shown [52] to have a *trans*-configuration like the familiar yellow powder form, their difference being due essentially to different crystal structures built up from the same (*trans*-) molecules.

Recently, it has been shown [53] by an *X*-ray analysis that the configuration of the 4-covalent compound of quadrivalent platinum, $Pt(CH_3)_3Cl$, is tetrahedral. This is a result of unusual interest, for it indicates that the principal valency of an atom may be a factor of importance in deciding the configuration of its 4-covalent derivatives.

F. G. Mann and D. Purdie [54] have published some valuable experimental data on the parachors of palladium and mercury in simple and complex compounds. They find that, in certain series of organo-metallic compounds, both simple and complex, the metal atom shows an apparent parachor which falls steadily as the homologous series is ascended, and may ultimately reach a constant value. For example, in the homologous series $(SR_2)_2PdCl_2$, the parachor of palladium fell from 36 for the methyl to -7 for the *n*-amyl compound. Another point of interest has arisen in this investigation. The dipole moments of the three ethyl compounds of the chloro-series $(SR_2)_2PdCl_2$, $(PR_3)_2PdCl_2$, and $(AsR_3)_2PdCl_2$, *viz.*, 2·27, 1·05, 1·04 ($\times 10^{-18}$ e.s.u.), strongly support the assumption that they are all stable *trans*-compounds. The symmetrical *trans*-compounds should have a dipole moment closely approaching zero, whereas the *cis*-isomerides should have very high moments. This conclusion is in agreement with the *X*-ray and chemical evidence relating to the thio-ether compounds of platinous and palladous chlorides.[55]

G. T. Morgan,[56] in an address to the Chemical Society, has dealt with some important advances made in recent years in the study of the rarer elements. He is, himself, an outstanding leader in this field of work, and the results which he and his colleagues have accumulated form the main topic of the address. Certain seams of Northumbrian coal give an ash containing up to 1% of germanium and 0·05% of gallium, and G. R. Davies, working in the Teddington laboratories, has elaborated a process for the extraction of both these rare elements. The germanium is distilled over with acid as tetrachloride, whilst gallium trichloride remains. Rhenium has been extracted from Australian molybdenite by a lengthy process involving fractional volatilisation, and ultimate separation with organic reagents such as 8-hydroxyquinoline and dipyridyl. The address concludes with some reference to co-ordination compounds of ruthenium, and a plea for a wider investigation of the rarer elements ". . . for discoveries will from time to time be made in the application of these materials which will redound to the credit of our science, and the good of the community."

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[52] F. G. Mann, (Miss) D. Crowfoot, D. C. Gattiker, and (Mrs.) N. Wooster *J.*, 1935, 1642.

[53] E. G. Cox and K. C. Webster, *Z. Krist.*, 1935, [*A*], **90**, 561.

[54] *J.*, 1935, 1549.

[55] E. G. Cox, H. Saenger, and W. Wardlaw, *J.*, 1934, 182; *A.*, 1934, 397; H. D. K. Drew and G. H. Wyatt, *J.*, 1934, 56; *A.*, 1934, 284.

[56] *J.*, 1935, 554; *A.*, 716.

S. R. C.
W. W.

3. NON-FERROUS ALLOY SYSTEMS.

Progress in the knowledge of alloy systems has not previously been reviewed in these Reports. From the viewpoint of the metallurgist, the subject is a vast one, and it has been necessary for the purpose of this Report to restrict the field to certain aspects which are clearly of interest to chemists. The policy adopted has been to disregard a great amount of more or less isolated observations on particular alloys, and to describe what has been done during the last five years or so on the examination of non-ferrous alloy systems from the constitutional point of view, with special reference to the formation of intermetallic compounds. It is natural, therefore, that mainly binary systems are considered, and that much work of industrial importance, of interest to the metallurgist and the engineer, falls outside the scope of the Report.

Methods of Investigation.—Although thermal analysis and micrographical examination continue to be of fundamental importance in the study of equilibrium diagrams, there is evidence that more use is being made of the investigation of other properties of alloy systems as accessory means, and that such wider investigations have led to the reconstruction of some of the older diagrams. The salient features of these methods have been discussed by H. Scott,[1] J. L. Haughton,[2] and W. Guertler.[3] C. Sykes [4] has pointed out that the standard cooling-curve methods may give unreliable results when applied to transformations involving atomic rearrangement in a homogeneous solid solution, and has described a modified, double differential cooling-curve method.

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[1] *First Comm. New Internat. Assoc. Test. Mat.*, 1930, [*A*], 339.

[2] *Ibid.*, p. 316.

[3] *Proc. Zurich Congr. Internat. Assoc. Test. Mat.*, 1932, **1**, 469.

[4] *Proc. Roy. Soc.*, 1935, [*A*], **148**, 422; *A.*, 576.

Outstanding among the more modern methods is the *X*-ray determination of alloy equilibrium diagrams. The value of the *X*-ray method has been emphasised by A. Westgren,[5] inasmuch as it makes possible, not only the determination of the nature of the crystal structure and dimensions of the crystal lattice of the different phases existing in the alloy system, but also the fixing of the position of the phase limits. There is the further advantage that some insight into the chemical characteristics of the phases is given, which the earlier metallographic methods could do only very incompletely.

The value of the electrical conductivity method has been discussed by W. Hume-Rothery; [6] advantages are claimed in the detection of very small ranges of solid solubility and in the fixing of phase transformations which are combined with hysteresis or small thermal effects. The theory of the electrical conductivity of alloys has been discussed,[7] and the rule that the atomic increase in resistance is greater as the distance between the elements in the periodic system increases has been confirmed for a series of gold alloys.

The study of constitution by magnetic measurements has been reviewed by A. Kussman,[8] G. Grube,[9] and E. Vogt.[10] The magnetic method has been used in the study of a series of alloy systems,[11] and the existence of the compounds SnSb, CdSb, ZnSb, and Sn_2Tl indicated by abrupt changes in the slope of the susceptibility–composition curves. Y. Shimizu [12] has directed attention to the great effect of adsorbed gases on magnetic susceptibility results, and it appears that the curious results obtained in some of the earlier investigations are due to the neglect to melt and anneal in a vacuum. Shimizu found that, in alloys which form continuous solid solutions, the maximum deviation of susceptibility from the values calculated from the additive rule is small. With eutectic alloys, with solubility on both sides, the susceptibility–composition curve is linear in the range of eutectic composition and slightly curved in the range of solid solution. The magnetic susceptibility–composition curves for several alloy systems of gold[13] and copper[14] have also been determined.

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[5] *Z. Metallk.*, 1930, **22**, 368; *Trans. Amer. Inst. Min. Met. Eng.*, Inst. Metals Div., 1931, 13; *Angew. Chem.*, 1932, **45**, 33; *Proc. Zurich Congr. Internat. Assoc. Test. Mat.*, 1932, **1**, 484; *B.*, 1931, 978.

[6] *Metallwirt.*, 1929, **8**, 1243; *A.*, 1930, 1106.

[7] G. Grube and J. Hille, *Z. anorg. Chem.*, 1930, **194**, 179; *A.*, 1931, 158; L. W. Nordheim, *Physical Rev.*, 1930, [ii], **35**, 1430; *A.*, 1931, 1361.

[8] *Z. Metallk.*, 1934, **26**, 25; *B.*, 1934, 407.

[9] *Ibid.*, 1935, **27**, 194.

[10] *Ibid.*, p. 40.

[11] F. L. Meara, *Physical Rev.*, 1931, [ii], **37**, 467; *Physics*, 1932, **2**, 33; *A.*, 1932, 686.

[12] *Sci. Rep. Tôhoku Imp. Univ.*, 1932, **21**, 826; *A.*, 1933, 455.

A few papers report the application of electropotential measurements to the determination of constitution. F. Griengl and R. Baum[15] have constructed isopotential lines for the system gold–tin–mercury in a triangular phase diagram. Although the curves give no evidence of AuSn or $AuSn_2$, these compounds are indicated by discontinuities in potential in the binary system, suggesting that they are partly dissociated in mercury. Potential studies of thallium–bismuth alloys in fused acetates have been made,[16] and the existence of Bi_2Tl indicated. A. Glazunov[17] has made an interesting application of the electropotential method to the determination of the phase structure of metallic coatings by anodic dissolution. Since each phase has its own potential, which remains constant during its dissolution, the composition and thicknesses of the phases can be determined from the lengths of the individual potential values (horizontal positions in the graph) and the intervals between them, provided the course of the potential curves of the binary system in question be known. Thus the presence of Zn_3Fe and probably $ZnFe_3$ in hot-dipped zinc coatings on iron has been shown.

The interpretation of heats of mixture of molten metals has been undertaken by M. Kawakami,[18] who found that with a few exceptions heat is evolved when the metals form intermetallic compounds, whilst heat is absorbed when solid solutions are produced.

Optical properties have so far played little definite part in the examination of alloy systems. S. Ueno[19] has shown, however, that the curve of intensity of reflexion of silver–aluminium alloys has a maximum corresponding with the compound $AlAg_3$, a break at $AlAg_2$, and a minimum at the eutectic. Similar investigations of the alloys of aluminium with magnesium[20] indicate a high reflectivity for Mg_3Al_2.

The cementation method, in which the constituents are heated together in a vacuum at temperatures near the solidus, has been applied to several alloy systems by L. Loskiewicz[21] and has led to suggested modifications of the diagrams. It appears from this work that the formation of a eutectic during cementation is possible only at temperatures above the melting point of the eutectic. Cementation below the melting point can occur only when the cementing metal has a solid solubility in the metal to be cemented. By similar technique with aluminium alloys, M. Bosshard[22] has confirmed the existence of the ternary compounds $Al_6Fe_2Si_3$, Al_2Cu_2Fe, Al_5NiCu_2, and Al_6Mg_4Cu.

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[13] E. Vogt, *Ann. Physik*, 1932, [v], **14**, 1; *A.*, 1932, 907.

[14] H. F. Seemann, *Z. Metallk.*, 1932, **24**, 299.

[15] *Monatsh.*, 1932, **61**, 330; *A.*, 1933, 127.

[16] A. Ölander, *Z. physikal. Chem.*, 1934, [*A*], **169**, 260; *A.*, 1934, 954.

[17] *Trans. Faraday Soc.*, 1935, **31**, 1262.

[18] *Sci. Rep. Tôhoku Imp. Univ.*, 1930, **19**, 521; *A.*, 1932, 296.

[19] *Mem. Coll. Sci. Kyōtō Imp. Univ.*, 1930, **13**, 141; *A.*, 1930, 681.

[20] J. Wulff, *J. Opt. Soc. Amer.*, 1934, **24**, 223; *A.*, 1934, 1086.

[21] *Przegląd Gorniczo-Hutniczy*, 1929, **21**, 583; *Przegląd Techniczy*, 1930, **69**, 508.

Structure of the Phases.—Reference has been made to the value of *X*-ray analysis in the detection of phases and determination of their structure. G. Sachs[23] maintains that a transformation in alloys generally consists of two partial processes, *viz.*, change of lattice structure and rearrangement of the atoms, and shows that these processes can be studied separately by *X*-ray investigation. The kinetics of lattice transformation are governed by (1) thermal formation of nuclei and crystal growth (at high temperatures), (2) regular change of the lattice and crystal growth (at moderate temperatures), or (3) regular change of the lattice alone (at lower temperatures). The effect of thermal agitation on atomic rearrangement in alloys has been discussed by W. L. Bragg and E. J. Williams.[24] The ordered has a lower potential energy than the disordered structure, but thermal agitation promotes disorder. Order sets in abruptly at a critical temperature, and increases as the temperature is lowered, becoming complete only at absolute zero. The sudden onset of order causes a sharp inflexion in curves relating resistivity, lattice spacing, and specific heat with temperature. Such inflexions simulate a phase change, although actually there is no such change.

The effect of additions of one metal on the lattice structure of another has been studied.[25] W. Hume-Rothery[26] has shown that the addition of cadmium, indium, tin, or antimony to silver changes its lattice structure to an extent which is proportional to the valency of the added element. The question whether the change in lattice constants in the formation of solid solutions depends on the grain size has been debated.[27]

W. Hume-Rothery[28] pointed out that the compositions of the β-phases of many binary alloys are such that the ratio of valency electrons to atoms is approximately 3 : 2. The generalisation has been extended by A. J. Bradley [29] to the γ-phases of certain alloys, where the ratio of valency electrons to atoms is found to be 21 : 13. Similarly, the ratio for a number of ε-phases is 7 : 4. The validity of these rules has been confirmed [30] for a number of binary alloys of copper, silver, and gold. H. Perlitz [31] points out that, since the ratio is always greater than 1, a necessary condition for the existence of these structures is that one of the metals contributes at least 2 valency electrons and the other component contributes not more than 1 valency electron to the lattice structure. The possible systems of alloys that can be formed in accordance with these requirements have been worked out.

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[22] *Aluminium*, 1935, **17**, 477.

[23] *Z. Metallk.*, 1932, **24**, 241; *A.*, 1932, 1196.

[24] *Proc. Roy. Soc.*, 1934, [*A*], **145**, 699; *A.*, 1934, 954.

[25] E. R. Jette, *Amer. Inst. Min. Met. Eng.*, 1934, Tech. Publ. No. 560, 1—16; *A.*, 1935, 24.

[26] *Nature*, 1935, **135**, 1038; *A.*, 919.

[27] E. Schmid and G. Siebel, *Metallwirt.*, 1932, **11**, 685; *A.*, 1933, 1110; U. Dehlinger and P. Wiest, *ibid.*, 1933, **12**, 2; *A.*, 1934, 249.

[28] *J. Inst. Metals*, 1926, **35**, 295; *A.*, 1926, 356.

Resulting from the study of a large number of binary alloy systems, Hume-Rothery and his collaborators [32] have been able to show that, if the atomic diameter of the solute differs by more than about 14% from that of the solvent, the solid solution is restricted to a few atoms per cent.; but when the size factor is favourable a solid solution may be formed, in which the solubility limits generally obey valency laws, the solubility becoming less as the valency increases. Under these conditions the maximum solid solubility is determined mainly by the concentration of valency electrons, and this principle permits the approximate calculation of solubility limits in certain ternary alloys.

A new approach to the problem of the chemical bond between metals has been suggested by J. Dorfman.[33] Assuming that the atoms of copper, zinc, aluminium, and tin entering the nickel lattice become singly ionised, he calculates that the negative values of the magnetic moments of these foreign atoms correspond with the number of valency electrons left attached to the corresponding ion.

In an examination of the systems aluminium–copper, antimony–silver, cadmium–tin, cadmium–zinc, copper–silver, and lead–tin, D. Stockdale [34] found no evidence for his supposition that in a binary eutectic the atoms of the two elements are present in a simple ratio. Recently, however, he [35] has put forward a series of empirical rules, which, although not exact, are claimed to give more accurate results than the majority of those that have been obtained experimentally in this connexion. (1) In a saturated solid solution at the temperature of the eutectic or peritectic there is a simple integral relation between the numbers of solvent and solute atoms. (2) There is a similar relation in a saturated solid solution in contact with a second solid phase at the temperature of transformation of the second phase. (3) In copper- and silver-rich alloys the solubilities at the above two temperatures are simply related, and it is possible to predict the solubility at the lower temperature if that at the higher is known. (4) In a eutectic mixture the elements are present in a simple integral atomic ratio. (5) In a eutectic mixture the ratio of the numbers of atoms, irrespective of their kind, in the two phases is simple.

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[29] *Phil. Mag.*, 1928, [vii], **6**, 878; *A.*, 1929, 125.

[30] A. Westgren and G. Phragmén, *Trans. Faraday Soc.*, 1929, **25**, 379; *A.*, 1929, 987; A. Westgren and W. Ekman, *Arkiv Kemi, Min. Geol.*, 1930, [*B*], **10**, [ii], 1; *A.*, 1931, 900.

[31] *J. Chem. Physics*, 1933, **1**, 335; *Acta Comm. Tartuensis*, 1933, [*A*], **24**, (2), 1; *A.*, 1933, 118.

[32] W. Hume-Rothery, G. W. Mabbott, and K. M. C. Evans, *Phil. Trans.*, 1934, **233**, 1; *A.*, 1934, 725.

[33] *Nature*, 1932, **130**, 506. [34] *J. Inst. Metals*, 1930, **43**, 193; *A.*, 1930, 537.

[35] *Proc. Roy. Soc.*, 1935, [*A*], **152**, 81.

A different angle on related problems is provided by work on the atomic heats of alloyed metals in the form of solid solutions or intermetallic compounds.[36] In both cases deviations from the additive rule have been noted. In a comparison of the heat contents of 25 intermetallic compounds with the sum of the heat contents of their components at different temperatures,[37] an increase in the heat content of the compound was observed in 14 and a decrease in 8 compounds; in the remaining 3 compounds the difference changed its sign with change of temperature. If in all cases the heat content of the compound were greater than the sum of those of the components, the conclusion might be reached that the surplus heat content should correspond with the energy for the vibration of molecules, *i.e.*, the lattice of the intermetallic compounds would be built up of molecules, not of atoms. This is, however, not the case.

The volume changes accompanying the formation of intermetallic compounds have been studied.[38] Published data on the molecular volume of intermetallic compounds and on the atomic volumes of their component metals seem to show that metals which can be strongly compressed mechanically undergo a contraction when they enter into an intermetallic compound, whilst metals which are difficult to compress do not.

F. H. Jeffery[39] has applied an interesting thermodynamical method to the study of a number of binary alloy systems. He deduces for a two-component, two-phase system consisting of a solid and a liquid phase, each of which is a dilute solution of one metal in another, the relation $\log(1 - n') - \log(1 - n) = L/RT - L/RT_0$, where L is the latent heat of fusion of the solvent, T_0 the freezing point, R and T have their usual significance, n is the molar fraction of the solute in the liquid, and n' that in the solid solution. Application of this equation to solutions of lead in tin, tin in lead, and cadmium in tin shows that in all cases the solute is monatomic and no intermetallic compounds are present. In the copper–tin system thermodynamic considerations show that the α-phase consists, in both the solid and the liquid state, of a solution of Cu_4Sn in monatomic copper; the β-phase is a solid solution of monatomic tin in monatomic copper; the η-phase in the solid state is the compound Cu_3Sn, but in the liquid state it consists of a solution of Cu_4Sn in monatomic tin; the H-phase is a solid solution of Cu_3Sn in monatomic tin. When applied to the copper–zinc alloys, the method indicates that the liquid solutions in equilibrium with the α- and the β-solid solution consist of $CuZn_4$ dissolved in monatomic copper, that the α-solid solution consists of $CuZn_4$ dissolved in monatomic copper, and the β-solid solution of $CuZn_2$ in monatomic copper. The liquid and solid solutions in the copper–gold and copper–silver systems are derived from monatomic molecules of copper and gold or copper and silver, respectively. In the lead-rich lead–antimony alloys the existence of the compound Pb_2Sb dissolved in monatomic lead is indicated. The liquid and solid solution phases of copper–magnesium alloys consist of simple atoms of copper and magnesium; the existence of $MgCu_2$ and Mg_2Cu is also confirmed by the thermodynamical method. The thermodynamics of solid-solution alloys has also been treated by C. Wagner and W. Schottky [40] and by H. Seltz.[41]

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[36] J. A. Bottema and F. M. Jaeger, *Proc. K. Akad. Wetensch. Amsterdam*, 1932, **35**, 916, 929; *A.*, 1933, 18.

[37] G. Tammann and A. Rohmann, *Z. anorg. Chem.*, 1930, **190**, 227; *A.*, 1932, 986.

[38] W. Biltz, *Z. Metallk.*, 1934, **26**, 230; *A.*, 1935, 158.

[39] *Trans. Faraday Soc.*, 1930, **26**, 86, 587, 588; 1931, **27**, 136, 137, 188; 1932, **28**, 452, 455, 567, 705; 1933, **29**, 550; *A.*, 1930, 406, 1360, 1361; 1931, 418, 676; 1932, 566, 907, 989; 1933, 454.

Alloys of the Alkali and Alkaline-earth Metals.—The sodium–potassium equilibrium has been investigated under conditions of manipulation that exclude contact with air.[42] An unstable compound Na_2K and a eutectic containing 66 atoms % of potassium have been confirmed. Viscosity determinations of these alloys in the liquid phase at 125° show a maximum at the composition K_2Na, but give no inflexion to indicate the compound Na_2K.[43]

The solidification diagram of the sodium–rubidium system does not resemble that of the sodium–potassium alloys, and no evidence of the compound Na_2Rb was found.[44] A eutectic occurs at 75 atoms % of rubidium at $-4{\cdot}5°$. The curve tends to become horizontal in the vicinity of the composition corresponding with $NaRb_2$. In the sodium–cæsium system thermal analysis shows a new compound Na_2Cs, and a eutectic at 75 atoms % of cæsium and $-30°$.[45] The mutual solubilities of sodium and calcium have been determined.[46] Potassium and rubidium are completely miscible in the solid state; the liquidus and solidus are very close and show a flat minimum at 32·8°, corresponding with 66·6 atoms % of rubidium.[47]

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[40] *Z. physikal. Chem.*, 1930, [*B*], **11**, 163; *A.*, 1931, 157.

[41] *J. Amer. Chem. Soc.*, 1934, **56**, 307; *A.*, 1934, 365.

[42] E. Rinck, *Compt. rend.*, 1933, **197**, 49; *A.*, 1933, 771.

[43] R. Kremann, M. Pestemer, and H. Schreiner, *Rec. trav. chim.*, 1932, **51**, 557; *A.*, 1932, 800.

The system calcium–bismuth forms two compounds, Ca_3Bi_2 and $CaBi_3$. The alloys of this system are attacked by moist air.[48] Alloys of calcium with smaller amounts of zinc, aluminium, or magnesium have been prepared as greyish-white powders, which are readily attacked by exposure to air and moisture.[49] The calcium–gold system contains 6 compounds : Au_4Ca, Au_2Ca, Au_9Ca_{10}, Au_3Ca, Au_3Ca_4, and $AuCa_2$. Calcium is practically insoluble in solid gold, but at room temperature it dissolves 4—5 atoms % of gold.[50]

The lithium–silver alloys have been examined for the first time, the *X*-ray method being used. At 500° the metals react violently with evolution of heat. The existence of the compounds AgLi and $AgLi_3$ has been established. Since no alteration in the lithium or silver lattices was observed, it is concluded that solid solutions are not formed.[51] Similar experiments, coupled with thermal analysis, on the lithium–copper alloys give a quite different result, for no compounds or solid solutions are formed.[52] Thermal analysis and electrical-resistance measurements of lithium–cadmium alloys have confirmed the existence of LiCd and proved the existence of the hitherto unknown compounds $LiCd_3$ and Li_3Cd.[53] The compounds LiCd and $LiCd_3$ have been confirmed independently by *X*-ray analysis,[54] but Li_3Cd was not detected by this method. The compounds LiTl, Li_2Tl, Li_5Tl_2, Li_3Tl, and Li_4Tl have been detected by thermal analysis and electrical-resistance determinations.[55] Of these, Li_5Tl_2 and Li_3Tl can be melted without decomposing. Similar methods applied to alloys of lithium and bismuth show the existence of Li_3Bi and LiBi; [56] the latter is dimorphous.

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[44] E. Rinck, *Compt. rend.*, 1933, **197**, 1404; *A.*, 1934, 137.

[45] *Ibid.*, 1934, **199**, 1217; *A.*, 1935, 22.

[46] *Ibid.*, 1931, **192**, 1378; *A.*, 1931, 900.

[47] *Ibid.*, 1935, **200**, 1205; *A.*, 693.

[48] E. Kurzniec, *Bull. Acad. polonaise*, 1931, [*A*], 31; *A.*, 1931, 1118.

[49] J. Meyer and R. Goralczyk, *Z. angew. Chem.*, 1930, **43**, 149; *B.*, 1930, 330.

[50] F. Weibke and W. Bartels, *Z. anorg. Chem.*, 1934, **218**, 241; *A.*, 1934, 838.

[51] S. Pastorello, *Gazzetta*, 1930, **60**, 493; 1931, **61**, 47; *A.*, 1930, 1359; 1931, 418.

[52] *Ibid.*, 1930, **60**, 988; *A.*, 1931, 296.

[53] G. Grube, H. Vosskühler, and H. Vogt, *Z. Elektrochem.*, 1932, **38**, 869; *A.*, 1933, 18.

[54] A. Baroni, *Atti R. Accad. Lincei*, 1933, [vi], **18**, 41; *A.*, 1934, 137.

Copper Alloys.—Certain aspects of the copper–gold alloys have received much attention. The transformation of the alloy containing 50 atoms % of each metal, from the cubic face-centred lattice with irregular distribution of atoms to the tetragonal lattice with regular distribution, has been studied by *X*-ray analysis.[57] With falling temperature the transformation occurs in two steps: (1) change of the lattice symmetry from cubic to tetragonal, (2) transition from an irregular to a regular distribution of the atoms. The first step occurs rapidly and completely, the second slowly and incompletely. Thus an intermediate state is reached, which is characterised by a considerably increased hardness, tensile strength, and electrical resistance.[58] In this system the existence of AuCu and $AuCu_3$ has been confirmed.[59] A transformation in $AuCu_3$ has been studied.[60] In addition to the AuCu and the $AuCu_3$ transformation, J. L. Haughton and R. J. M. Payne [61] have found another transformation in alloys approximating to the composition of Au_2Cu_3. The compound Au_2Cu_3 is also indicated by the electrical conductivity and thermoelectric force curves of M. Le Blanc and G. Wehner,[62] but is denied by W. Broniewski and K. Wesolowski.[63]

W. R. D. Jones [64] obtained evidence of Mg_2Cu and $MgCu_2$, but not of MgCu. In spite of the old-established use of brasses, the equilibrium diagram of the copper–zinc alloys has not been unequivocally settled. Examination of numerous properties of a wide range of these alloys [65] has confirmed the existence of the compounds CuZn, $CuZn_2$, and $CuZn_6$, but not Cu_2Zn_3, Cu_2Zn,

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[55] G. Grube and G. Schaufler, *Z. Elektrochem.*, 1934, **40**, 593; *A.*, 1934, 1065.

[56] G. Grube, H. Vosskühler, and H. Schlecht, *ibid.*, p. 270; *A* 1934, 724.

[57] K. Oshima and G. Sachs, *Z. Physik*, 1930, **63**, 210; U. Dehlinger and L. Graf, *ibid.*, 1930, **64**, 359; *A.*, 1930, 1360; L. Graf, *Z. Metallk.*, 1932, **24**, 248; *A.*, 1932, 1196.

[58] E. Schuch, *Metallwirt.*, 1933, **12**, 145; *A.*, 1933, 1238.

[59] N. S. Kurnakow and N. W. Ageew, *J. Inst. Metals*, 1931, **46**, 481; *A.*, 1932, 1224.

[60] G. Sachs and J. Weerts, *Z. Physik*, 1931, **67**, 507; *A.*, 1931, 414.

[61] *J. Inst. Metals*, 1931, **46**, 457; *A.*, 1931, 1224.

[62] *Ann. Physik*, 1932, [v], **14**, 481; *A.*, 1932, 989.

[63] *Compt. rend.*, 1934, **198**, 370; *A.*, 1934, 248.

[64] *J. Inst. Metals*, 1931, **46**, 395; *A.*, 1931, 1224.

[65] W. Broniewski and J. Strasburger, *Compt. rend.*, 1930, **190**, 1412; *Rev. Mét.*, 1931, **28**, 19, 79; *Prace Zakladu Metall. Pol. Warsaw*, 1933, **3**, 3; *A.* 1930, 987.

$Cu_{14}Zn_{13}$, $Cu_{21}Zn_{31}$, Cu_3Zn_5, Cu_4Zn_9, or Cu_4Zn. On the other hand, C. Rossi [66] claims to have prepared single crystals of Cu_2Zn_3. The crystal structures of Cu_5Zn_8 and Cu_5Cd_8 have been compared.[67] The relation between mean atomic volume and composition in this series of alloys has been studied.[68] Examination of the electrical properties of the copper–cadmium alloys suggests the existence of $CuCd_3$, Cu_2Cd_3, Cu_4Cd_3, and possibly Cu_2Cd.

The copper–gallium system has been investigated; [69] it contains 7 intermediate phases, including Cu_3Ga and Cu_9Ga_4. The copper–indium system is somewhat similar [70] and contains the compounds Cu_4In, Cu_9In_4, and Cu_2In.

Work continues on the copper–tin series.[71] Further evidence that the δ-phase is $Cu_{31}Sn_8$, not Cu_4Sn, has been obtained,[72] whilst the ε-phase, formerly written as CuSn, is confirmed as Cu_6Sn_5.[73] It has also been shown that an alloy, identical with Cu_3Sn prepared by fusion, is produced by the action of tin on copper sulphate solutions under certain conditions.[74] Equilibria in the ternary systems of copper and tin with nickel,[75] manganese,[76] lead,[77] or beryllium [78] have been investigated.

Silver Alloys.—X-Ray analysis has confirmed the existence of AgCa and Ag_3Ca, but not of Ag_4Ca, Ag_2Ca, or $AgCa_2$, formerly claimed.[79] By the thermal method, the existence of Ag_4Sr, Ag_5Sr_3, AgSr, and Ag_2Sr_3 and also of Ag_4Ba, Ag_3Ba_2, and Ag_5Ba_3 is indicated.[80]

The lattice parameters and densities of solid solutions of aluminium in silver have been measured.[81] The experimental densities are slightly lower than those calculated on the basis of a direct substitution of aluminium for silver atoms in the silver lattice, and it is concluded that the aluminium in the solid solution must be combined chemically with the adjacent silver. Re-examination of this system by thermal analysis [82] shows three compounds: Ag_3Al, Ag_3Al_2, and Ag_2Al.[83] The solid solubility of indium in silver is 19·4% at room temperature. The system contains the compounds Ag_3In, Ag_5In_2, and $AgIn_3$.[84] The system silver–praseodymium contains Ag_3Pr, Ag_2Pr, and $AgPr$.[85] The ternary systems of silver and zinc with copper or aluminium,[86] and of silver and antimony with zinc, cadmium, or copper [87] have been investigated, and similar types of alloys have been examined from the viewpoint of an improved, untarnishable sterling silver.[88]

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[66] *Z. Physik*, 1932, **74**, 707; *A.*, 1932, 454.

[67] A. J. Bradley and C. H. Gregory, *Phil. Mag.*, 1931, [vii], **12**, 143; *A.*, 1931, 896.

[68] E. A. Owen and L. Pickup, *Proc. Roy. Soc.*, 1933, [*A*], **140**, 179; *A.*, 1933, 454.

[69] F. Weibke, *Z. anorg. Chem.*, 1934, **220**, 293; *A.*, 1935, 22.

[70] F. Weibke and H. Eggers, *ibid.*, p. 273; *A.*, 1935, 22.

[71] J. Verö, *Z. anorg. Chem.*, 1934, **218**, 402; *A.*, 1934, 953.

[72] M. Hamasumi and S. Nishigori, *Tech. Rep. Tôhoku*, 1931, **10**, 131; *A.*, 1931, 900.

[73] M. Hamasumi, *Kinz. no Kenk.*, 1933, **10**, 137.

[74] H. Kersten and J. Maas, *J. Amer. Chem. Soc.*, 1933, **55**, 1002; *A.*, 1933, 454.

[75] J. T. Eash and C. Upthegrove, *Trans. Amer. Inst. Min. Met. Eng.*, 1933, **104**, 221; *A.*, 1933, 119; J. Verö, *Mitt. Berg. Hütten. Abt. Hochschule, Sopron*, 1932, **4**, 1.

[76] *Idem, ibid.*, 1933, **5**, 1; *A.*, 1934, 1301.

[77] *Idem, ibid.*, 1932, **4**, 1.

[78] E. S. Rowland and C. Upthegrove, *Amer. Inst. Min. Met. Eng.*, 1935, Tech. Publ. No. 613; *A.*, 1935, 1066.

[79] C. Dégard, *Z. Krist.*, 1935, **90**, 399; *A.*, 1198.

[80] F. Weibke, *Z. anorg. Chem.*, 1930, **193**, 297; *A.*, 1930, 1509.

Magnesium Alloys.—A new diagram for the magnesium–zinc alloys [89] shows the compounds $MgZn_5$, $MgZn_2$, and $MgZn$.

X-Ray investigation of magnesium–cadmium alloys containing 30—80 atoms % of magnesium has confirmed the existence of $MgCd_3$ and Mg_3Cd, but not $MgCd_2$.[90] The equilibrium diagram of the magnesium–thallium system has been revised.[91] Earlier investigations had suggested the existence of the compounds Tl_3Mg_8, $TlMg_2$, and Tl_2Mg_3. Of these only $TlMg_2$ has been confirmed, the others appearing to be eutectics. In addition, Tl_2Mg_5 and $TlMg$ are considered to exist. The alloys with praseodymium include two well-defined compounds, $MgPr$ and Mg_2Pr, and probably $MgPr_4$.[92] Electrical-conductivity measurements of magnesium-rich alloys with tin show a minimum at the composition corresponding with Mg_2Sn.[93] The magnesium–antimony system contains only one compound Mg_3Sb_2, which is dimorphous, having a transformation temperature at 930° ± 2°.[94] The solid solubility of nickel in magnesium is less than 0·1%.[95] Ternary systems investigated include magnesium–aluminium–copper,[96] magnesium–zinc–silicon,[97] and magnesium–zinc–calcium.[98]

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[81] R. T. Phelps and W. P. Davey, *Amer. Inst. Min. Met. Eng.*, 1931, Tech. Publ. No. 443, 1.

[82] F. E. Tischtckenko, *Zhur. Obs. Khim.*, 1933, **3**, 549; *A.*, 1934, 21.

[83] Cf. N. Ageew and D. Shoyket, *J. Inst. Metals*, 1933, **52**, 119; *A.*, 1933, 1110.

[84] F. Weibke and H. Eggers, *Z. anorg. Chem.*, 1935, **222**, 145; *A.*, 576.

[85] G. Canneri, *Met. Ital.*, 1934, **26**, 794.

[86] S. Ueno, *Mem. Coll. Sci. Kyōtō Imp. Univ.*, 1929, **12**, 347; 1930, **13**, 91; *A.*, 1930, 284, 535.

[87] W. Guertler and W. Rosenthal, *Z. Metallk.*, 1932, **24**, 7, 30; *A.*, 1932, 455.

[88] K. W. Ray and W. N. Baker, *Ind. Eng. Chem.*, 1932, **24**, 778; *B.*, 1932, 845; L. Guillet, A. Petit, and J. Cournot, *Rev. Mét.*, 1932, **29**, 113, 183; *B.*, 1933, 393.

[89] A. A. Botschvar and I. P. Velitschko, *Z. anorg. Chem.*, 1933, **210**, 164; *A.*, 1933, 219.

[90] U. Dehlinger, *ibid.*, 1930, **194**, 223; *A.*, 1931, 157.

[91] G. Grube and J. Hille, *Z. Elektrochem.*, 1934, **40**, 101; *A.*, 1934, 356.

[92] G. Canneri, *Met. Ital.*, 1933, **25**, 250; *A.*, 1934, 483.

Mercury Alloys.—Evidence that dilute liquid amalgams are colloidal sols in which mercury acts as dispersion medium has been obtained in amalgams of sodium,[99] copper and silver,[1] and iron.[2]

Thermal analysis of the rubidium–mercury system indicates the compounds Rb_3Hg_4, $RbHg_2$, Rb_2Hg_7, Rb_5Hg_{18}, Rb_2Hg_9, $RbHg_6$, $RbHg_9$, and Rb_7Hg_8.[3] Comparison with other mercury–alkali metal systems shows that the affinity for mercury increases as the atomic weight of the alkali metal increases, and the compounds formed are more complex. The constitution of silver amalgams has been determined; [4] *X*-ray investigation shows the presence of Ag_3Hg_4.[5]

The compounds Li_6Hg, Li_3Hg, Li_2Hg, LiHg, $LiHg_2$, and $LiHg_3$ have been detected in lithium amalgams by thermal analysis [6] and confirmed by *X*-rays.[7] Only Li_3Hg and LiHg can be melted unchanged. Although thermal analysis and microscopical examination have given no evidence of compound formation in cadmium amalgams, *X*-ray analysis indicates that Cd_3Hg exists.[8]

Determinations of the parachor of thallium dissolved in mercury show that it is not in the monatomic state, but is combined with mercury or other thallium atoms to form polyatomic molecules.[9] The solid thallium amalgams have been examined by the *X*-ray method.[10] There is evidence that many rare-earth metals form compounds with mercury of the type MHg_4.[11]

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[93] G. Grube and H. Vosskühler, *Z. Elektrochem.*, 1934, **40**, 566; *A.*, 1934, 1065.

[94] G. Grube and R. Bornhak, *ibid.*, 1934, **40**, 140; *A.*, 1934, 590.

[95] J. L. Haughton and R. J. M. Payne, *J. Inst. Metals*, 1934, **54**, 275; *A.*, 1934, 590.

[96] A. Portevin and P. Bastien, *Compt. rend.*, 1932, **195**, 441; *A.*, 1932, 989; *Chim. et Ind.*, 1934, Special No., 490; *A.*, 1934, 725.

[97] E. Elchardus and P. Laffitte, *Compt. rend.*, 1933, **197**, 1125; *A.*, 1934, 22.

[98] R. Paris, *ibid.*, 1933, **197**, 1634; *A.*, 1934, 138.

[99] G. R. Paranjpe and R. M. Joshi, *J. Physical Chem.*, 1932, **36**, 2474; *A.*, 1932, 1196; H. E. Bent, *ibid.*, 1933, **37**, 431; *A.*, 1933, 561.

[1] R. Köhler, *Kolloid-Z.*, 1933, **64**, 200; *A.*, 1933, 895.

[2] N. M. Tchuiko, *Ukrain. Chem. J.*, 1931, **6**, 229.

[3] W. Biltz, F. Weibke, and H. Eggers, *Z. anorg. Chem.*, 1934, **219**, 119; *A.* 1934, 1064.

[4] A. J. Murphy, *J. Inst. Metals*, 1931, **46**, 507; *A.*, 1931, 1224.

[5] A. Weryha, *Z. Krist.*, 1933, **86**, 335; *A.*, 1934, 16.

[6] G. Grube and W. Wolf, *Z. Elektrochem.*, 1935, **41**, 675; *A.*, 1314.

[7] E. Zintl and A. Schneider, *ibid.*, 1935, **41**, 771.

[8] N. W. Taylor, *J. Amer. Chem. Soc.*, 1932, **54**, 2713; *A.*, 1932, 989.

[9] L. Belladen and A. Triolo, *Gazzetta*, 1934, **64**, 461.

The solubility of iron in mercury at 20° is 0·00007% ; and that of nickel 0·00014% (by wt.).[12] The solubility of gold in mercury at 280—400° has been determined; the gold-rich compound is probably Au_3Hg.[13] An *X*-ray investigation of alloys of mercury with gold, silver, or tin has been carried out.[14] The system mercury–manganese–tin has been studied.[15]

A considerable number of binary, ternary, and quaternary compounds of metals such as copper, tin, zinc, and iron with or without mercury have been obtained by A. S. Russell and his collaborators [16] by reaction in mercury.

A technique for determining the vapour pressure of amalgams has been described and applied to amalgams of the alkali metals.[17]

Aluminium Alloys.—Much of the work on aluminium alloys concerns their properties for structural purposes and is of interest mainly to metallurgists and engineers. A summary of available information on the constitution of binary alloys of aluminium has been given by E. T. Richards.[18]

The solubility of sodium in molten aluminium has been determined ; there is no evidence of solid solubility,[19] nor has a solid solubility of barium in aluminium been detected.[20] *X*-Ray examination has established one compound Al_4Ba in the aluminium–barium system.[21]

The solid solubilities of beryllium [22] and magnesium [23] in aluminium have been determined. An investigation of the aluminium–magnesium alloys shows that the two metals are mutually soluble in the solid state and can form the compounds Al_8Mg_5, AlMg, and Al_3Mg_4.[24] G. Wassermann [25] has shown that the lattice parameter of aluminium is increased by about 0·0045 Å. for every 1 atom % of magnesium added, and by about 0·001 Å. for every 1 atom % of zinc. Further *X*-ray work indicates that the supposed compound Al_2Zn_3 does not exist.[26]

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[10] A. Ölander, *Z. physikal. Chem.*, 1934, [*A*], **171**, 425; *A.*, 1935, 440.

[11] P. T. Daniltchenko, *Zhur. Obs. Khim.*, 1931, [*A*], **163**, 467; *A.*, 1931, 1381.

[12] E. Palmaer, *Z. Elektrochem.*, 1932, **38**, 70; *A.*, 1932, 330.

[13] J. T. Anderson, *J. Physical Chem.*, 1932, **36**, 2145.

[14] S. Stenbeck, *Z. anorg. Chem.*, 1933, **214**, 17; *A.*, 1933, 1006.

[15] A. N. Campbell and H. G. Carter, *Trans. Faraday Soc.*, 1933, **29**, 1295; *A.*, 1934, 138.

[16] *Nature*, 1930, **125**, 89; 1934, **133**, 217; *J.*, 1932, 841, 852, 857; 1934, 1750; *A.*, 1930, 177; 1932, 456, 1083; 1934, 265.

[17] J. S. Pedder and S. Barratt, *J.*, 1933, 537; *A.*, 1933, 669; H. H. von Halban, jun., *Helv. Physica Acta*, 1935, **8**, 65.

[18] *Metallbörse*, 1935, **25**, 498, 530, 562, 721, 1041.

[19] E. Scheuer, *Z. Metallk.*, 1935, **27**, 83; *A.*, 928.

[20] E. Alberti, *ibid.*, 1934, **26**, 6; *A.*, 1934, 482.

[21] K. R. Andreas and E. Alberti, *ibid.*, 1935, **27**, 126; *A.*, 1065.

[22] M. Haas and D. Uno, *ibid.*, 1930, **22**, 277; *B.*, 1930, 1072.

[23] E. Schmid and G. Siebel, *ibid.*, 1931, **23**, 202; *B.*, 1931, 978.

[24] M. Kawakami, *Kinzoku no Kenkyu*, 1933, **10**, 532.

[25] *Z. Metallk.*, 1930, **22**, 158; *B.*, 1930, 717.

N. A. Pushin and V. Stajić [27] claim to have detected the compounds Al_2Ga, AlGa, and $AlGa_2$, but this claim is not substantiated by the experiments of E. Jenckel.[28] In the system aluminium–praseodymium [29] the compounds PrAl, $PrAl_2$, and $PrAl_4$ are said to exist, the last in two modifications. A revision of the diagram for aluminium-rich aluminium–titanium alloys has been undertaken, and the compound $TiAl_3$ confirmed.[30] It has been shown [31] that variations in casting temperature and rate of cooling determine whether the $TiAl_3$ in these alloys separates out as needles or remains so highly dispersed that the alloy behaves as a solid solution.

The solid solubility of antimony in aluminium is less than 0·1% ;[32] only one compound, AlSb, is formed in this system. The compound decomposes in moist air.[33]

Dissolution in dilute hydrochloric acid of an aluminium alloy containing 1·4% of chromium leaves a residue of rhombohedral plates of $CrAl_7$.[34] In the aluminium–manganese system, A. J. Bradley and P. Jones [35] detected by *X*-rays the compounds Al_7Mn and Al_3Mn. Since small amounts of iron profoundly affect the equilibria, this system has been re-examined, metals of very high purity being used.[36] The solid solubility of manganese in aluminium was determined, and the existence of Al_6Mn and Al_4Mn established. An investigation of the system aluminium–cobalt [37] shows that the solid solubility of cobalt in aluminium is very small. A eutectic at 1·45% of cobalt was observed. When the aluminium-rich alloys are treated with dilute acids, a residue having the formula Co_2Al_9 is obtained.

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[26] E. Schmid and G. Wassermann, *Z. Metallk.*, 1934, **26**, 146; *A.*, 1934, 1064.

[27] *Z. anorg. Chem.*, 1933, **216**, 26; *A.*, 1934, 138.

[28] *Z. Metallk.*, 1934, **26**, 249.

[29] G. Canneri, *Alluminio*, 1933, **2**, 87.

[30] W. L. Fink, K. R. van Horn, and P. M. Budge, *Amer. Inst. Min. Met. Eng.*, 1931, Tech. Publ. No. 393, 1; *A.*, 1931, 676.

[31] H. Bohner, *Z. Metallk.*, 1934, **26**, 268.

[32] E. H. Dix, jun., F. Keller, and L. A. Willey, *Amer. Inst. Min. Met. Eng.*, 1930, Tech. Publ. No. 356, 1; *A.*, 1931, 158.

[33] J. Veszelka, *Mitt. Berg. Hütten. Abt. Hochschule, Sopron*, 1931, **3**, 193; *A.*, 1932, 1082.

[34] W. L. Fink and H. R. Freche, *Trans. Amer. Inst. Min. Met. Eng.*, Inst. Metals Div., 1933, **104**, 325.

[35] *Phil. Mag.*, 1931, [vii], **12**, 1137; *A.*, 1932, 116.

[36] E. H. Dix, jun., W. L. Fink, and L. A. Willey, *Trans. Amer. Inst. Min. Met. Eng.*, Inst. Metals Div., 1933, **104**, 335.

[37] W. L. Fink and H. R. Freche, *Amer. Inst. Min. Met. Eng.*, 1932, Tech. Publ. No. 473, 1; *A.*, 1932, 683.

Ternary systems, the constitutions of which have been investigated, include aluminium–magnesium–silicon,[38] aluminium–copper–silicon,[39] aluminium–iron–silicon,[40] aluminium–antimony–magnesium,[41] aluminium–silver–magnesium,[42] and aluminium–nickel–tin.[43]

Tin Alloys.—The equilibrium diagrams of all the known binary alloys of tin have been compiled and annotated by E. S. Hedges and C. E. Homer.[44] *X*-Ray analysis of the tin–gold system confirms the existence of AuSn, $AuSn_2$, and $AuSn_4$.[45] Thermal investigation of tin–lithium alloys indicates the existence of $SnLi_4$, Sn_2Li_3, and Sn_4Li; *X*-ray analysis confirms the first two, but not the last.[46] Other thermal and electrical conductivity measurements in this system demonstrate the compounds $SnLi_4$, Sn_2Li_7, Sn_2Li_5, $SnLi_2$, SnLi, and Sn_2Li. The solid solubility of lithium in tin is inappreciable.[47] Tin–barium alloys have been prepared by electrolysis of eutectic mixtures of barium and potassium chlorides with a molten tin cathode.[48] The system contains the compounds Sn_3Ba and Sn_5Ba. Tin–strontium alloys have been prepared by a similar method, and the compounds Sn_3Sr and Sn_5Sr identified.[49]

The tin–arsenic alloys have been investigated by *X*-rays.[50] There is a wide range of solid solubility at both ends of the series; the compound SnAs exists, but not Sn_3As_2. Several *X*-ray investigations of the tin–antimony system have been made.[51] The compound formed is definitely SnSb, not Sn_3Sb_2. Single crystals of this compound have been obtained.[52] The tin–bismuth system has been examined by the *X*-ray method.[53] A marked effect of bismuth in refining the grain size of tin has been noted.[54]

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[38] L. Losana, *Met. Ital.*, 1931, **23**, 375; *A.*, 1932, 907; E. H. Dix, jun., F. Keller, and R. W. Graham, *Amer. Inst. Min. Met. Eng.*, 1930, Tech. Publ. No. 357, 1; *A.*, 1931, 158.

[39] G. G. Urazov, S. A. Pogodin, and G. M. Zomornev, *Min. Syrie i Zvet. Metally*, 1929, **4**, 160.

[40] V. Fuss, *Z. Metallk.*, 1931, **23**, 231; *B.*, 1931, 929.

[41] E. Loofs-Rassow, *Hauszeit. V.A.W.u.d. Erftwerk A.G. Aluminium*, 1931, **3**, 20; *B.*, 1931, 1143.

[42] B. Otani, *Kinzoku no Kenkyu*, 1933, **10**, 262.

[43] S. Kato, *Suiyokai-Shi*, 1931, **6**, 529; *A.*, 1932, 567.

[44] Internat. Tin Res. and Dev. Council, 1935, Tech. Publ. *B.*, No. 2, 1—90; *A.*, 1065.

[45] S. Stenbeck and A. Westgren, *Z. physikal. Chem.*, 1931, [*B*], **14**, 91; *A.*, 1931, 1223.

[46] A. Baroni, *Atti R. Accad. Lincei*, 1932, [vi], **16**, 153; *A.*, 1933, 18.

[47] G. Grube and E. Meyer, *Z. Elektrochem.*, 1934, **40**, 771; *A.*, 1935, 23.

[48] K. W. Ray, *Metals and Alloys*, 1930, **1**, 314; *A.*, 1930, 681.

[49] *Idem*, *Ind. Eng. Chem.*, 1930, **22**, 519; *B.*, 1930, 866.

[50] W. H. Willott and E. J. Evans, *Phil. Mag.*, 1934, [vii], **18**, 114; *A.*, 1934, 953.

[51] W. M. Jones and E. G. Bowen, *Nature*, 1930, **126**, 840; *Phil. Mag.*, 1931, [vii], **12**, 441; *A.*, 1931, 33; K. Iwasé, N. Aoki, and A. Ôsawa, *Sci. Rep. Tôhoku Imp. Univ.*, 1931, **20**, 353; *A.*, 1931, 1364.

The solid solubility of silver, copper, or nickel in tin is very small.[55] No intermetallic compound has been found in the tin–cadmium system.[56]

Re-examination of the tin–iron system [57] gives no evidence of Fe_3Sn, but shows the compounds Fe_2Sn, FeSn, and $FeSn_2$. These compounds have been confirmed independently by W. F. Ehret and A. F. Westgren [58] and by W. D. Jones and W. E. Hoare.[59] $FeSn_2$, but no other tin–iron compound, occurs in tin-plate.[60]

Lead Alloys.—With calcium, the compounds Pb_3Ca and PbCa are formed.[61] A complete equilibrium diagram for the lead–lithium system has been established; the compounds PbLi, Pb_2Li_5, $PbLi_3$, Pb_2Li_7, and $PbLi_4$ are formed.[62]

Lead and germanium do not form solid solutions or compounds.[63] No compound of lead with arsenic is formed, and the solid solubility of arsenic in lead is only about 0·01% at room temperature.[64] There is no evidence for the formation of a solid solution of antimony in lead, or of any definite compound in the series.[65]

An outstanding achievement in lead alloys is the improvement of mechanical properties and corrosion resistance of lead by the addition of a small amount of tellurium.[66]

E. S. H.
S. R. CARTER.
E. S. HEDGES.
W. WARDLAW.

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[52] H. S. van Klooster and M. O. Debacher, *Metals and Alloys*, 1933, **4**, 23; *A.*, 1933, 344.

[53] D. Solomon and W. M. Jones, *Phil. Mag.*, 1931, [vii], **11**, 1090; *A.*, 1931, 676.

[54] A. A. Botchvar and N. E. Merkurjew, *Z. anorg. Chem.*, 1933, **210**, 161; *A.*, 1933, 219; D. Hanson and E. J. Sandford, *J. Inst. Metals*, 1935, **56**, 191.

[55] D. Hanson, E. J. Sandford, and H. Stevens, *ibid.*, 1935, **55**, 115.

[56] D. Hanson and W. T. Pell-Walpole, *ibid.*, 1935, **56**, 165; *A.*, 1935, 440.

[57] C. A. Edwards and A. Preece, *J. Iron Steel Inst.*, 1931, **124**, 41; *B.*, 1931, 1053.

[58] *J. Amer. Chem. Soc.*, 1933, **55**, 1339; *A.*, 1933, 562.

[59] *J. Iron Steel Inst.*, 1934, **129**, 273; *A.*, 1934, 724.

[60] W. E. Hoare, *ibid.*, 1934, **129**, 253; *B.*, 1934, 581.

[61] R. R. Syromiatnikov, *Metallurg.*, 1931, **6**, 466.

[62] G. Grube and H. Klaiber, *Z. Elektrochem.*, 1934, **40**, 745.

[63] T. R. Briggs and W. S. Benedict, *J. Physical Chem.*, 1930, **34**, 173; *A.*, 1930, 284.

[64] O. Bauer and W. Tonn, *Z. Metallk.*, 1935, **27**, 183.

[65] D. Solomon and W. M. Jones, *Phil. Mag.*, 1930, [vii], **10**, 470; *A.*, 1930, 1359.

[66] W. Singleton and B. Jones, *J. Inst. Metals*, 1933, **51**, 71; *B.*, 1933, 351.

CRYSTALLOGRAPHY.
(1934—1935.)

CRYSTAL PHYSICS.

The Electron Theory of Metals.—It has long been known that the characteristic structure of certain alloys is determined not so much by its composition as by the ratio of the total number of valency electrons to the total number of atoms in the unit cell. Thus, the characteristic complex structure of γ-brass is shared by the alloys Cu_5Zn_8, Cu_9Al_4, Cu_3Sn_8, Ni_5Zn_{21}, and many others which all have in common an electron : atom ratio of 21 : 13. Similarly, the structure of β-brass corresponds to an electron : atom ratio of 3 : 2, and that of ε-brass to a ratio of 7 : 4. These ratios, first put forward on empirical grounds by Hume-Rothery in 1927, have recently been given a quantum-mechanical explanation by H. Jones.[1] An attempt is here made to give an elementary physical picture which will convey the essential features of the theory.

The state of an electron may be completely defined in terms of the three co-ordinates k_x, k_y, and k_z of its momentum. If we imagine these co-ordinates to be plotted along three rectangular axes, the state of the electron is described by the point (k_x, k_y, k_z) in the momentum space thus defined. If the electron is free, the energy associated with the state is proportional to the square of the momentum, *i.e.*, to the square of the vector joining the point in question to the origin of momentum space. On account of the quantum conditions and the exclusion principle, no two electrons may exist in the same state, so that each electron requires for itself a definite volume of momentum space, and an assemblage of many electrons will occupy a spherical domain whose size is determined by the number of electrons considered. If the electrons are not free, as will be the case in a crystal where we must take into account the effect of the lattice field, it can be shown that the energy of the electron no longer varies continuously with the momentum, but that there are certain planes in momentum space such that when the point describing the state of the electron crosses one of these planes a discontinuous energy change takes place.[2] The electrons in the neighbourhood of a discontinuity are those whose wave-length and direction would lead them to be reflected by the corresponding plane of the crystal. Just below the plane the energy is abnormally depressed; just above it, abnormally raised. Between successive planes the energy varies continuously with momentum and approximates to that of a free electron. It may be shown, further, that the planes in momentum space across which these energy discontinuities take place are parallel to all possible crystallographic planes in the crystal, so that in the case of *e.g.*, a cubic substance, the origin is surrounded by a series of concentric zones successively bounded by the faces of the cube, the dodecahedron, the octahedron, and so on. The magnitude of the energy jump across the various zones is not constant, but is proportional to the degree of scattering of electron waves from the corresponding plane in the crystal, and therefore closely related to the intensity of the *X*-ray reflexion: if all the atoms in the structure have nearly the same atomic number, it is actually proportional to the amplitude of this reflexion.

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[1] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 225; *A.*, 1934, 483.

[2] Brillouin, " Quantenstatistik," Chap. 8; A. Sommerfeld and H. A. Bethe, " Handbuch der Physik," XXIV, 2.

In the γ-alloys, experiment shows that, of the planes with small indices, only those of the forms $\{411\}$ and $\{330\}$ give rise to strong *X*-ray reflexion. We therefore conclude that the first planes in momentum space outwards from the origin across which the energy shows an appreciable discontinuity are those lying parallel to faces of these two forms. The figure bounded by these two forms is a polyhedron of 36 faces, not very far from spherical in shape.

Let us now imagine that the number of electrons in the structure is gradually increased from zero. At first, the Fermi distribution, *i.e.*, the volume occupied by the states of the electrons in momentum space, will grow very nearly spherically until it comes into proximity with the faces of the zonal polyhedron. When the sphere touches the zone, the distribution will no longer grow in that particular direction, since to do so would correspond to a large energy increment, but rather in other directions in which growth can still take place without the zone being crossed. The distribution will therefore ultimately assume a distorted shape approximating to that of the zone. Jones has calculated that in the case of the γ-alloys, for a unit cell containing 52 atoms, the spherical Fermi distribution inscribed in the zonal polyhedron corresponds to 80 electrons, whereas the whole polyhedron would hold 90. The actual number of electrons in the unit cell is 84, so that in the γ-alloys the surface of the Fermi distribution lies very close to the surface of energy discontinuity. This Jones states to be the distinguishing feature of the γ-structures. The exact filling of the zone corresponds to lowering of the energy of the lattice relative to other lattices with a different zone arrangement, and consequently adds stability to the structure. In terms of the theory of diamagnetic susceptibility given by R. Peierls,[3] it accounts for the remarkably large diamagnetic susceptibilities of the γ-alloys, and it also gives an explanation of the large Hall coefficient which these alloys show.

H. Jones[4] has now extended the theory to the case of ϵ- and η-phases, and has succeeded in accounting for the observed variation of the axial ratio with composition in these phases and also for the range of composition over which the phase is stable. In these cases, and also in the case of bismuth, there is a very small but finite ' overlap ' of the Fermi distribution beyond the first Brillouin zone. From this, the diamagnetic susceptibilities of bismuth and some of its alloys, and also the magnetostriction, are deduced in good agreement with experiment.

The application of the theory to the β-phase has been considered by U. Dehlinger,[5] who shows that in this case the first zone is only partially filled, since the number of electrons which it would accommodate is two per atom whereas the observed electron : atom ratio is 3 : 2. This, according to Dehlinger, corresponds to the fact that β-phases are stable only at high temperatures.

As the result of these theoretical advances, we are now in a position to get a general view of metal chemistry and its relation to the other parts of chemistry. Such a picture has been given by F. Hund.[6] In it, electrons are pictured as occupying bonding and anti-bonding states. If each atom brings so few electrons that only part of the former are filled, the result is a metal of the general A type of alkalis and alkaline earths. When the bonding zone is exactly filled, the result is an insulator of the type of diamond. If part of the next anti-bonding zone is filled, the result will be again a metal, but of the B type of bismuth or tellurium (the electrons of course can be used to form a closed shell molecule as in red selenium, Se_8, or yellow phosphorus, P_4). Finally, if both zones are filled, the result is again an insulator, this time a rare gas.

The theory of the A type metals is fairly satisfactory. E. Wigner and F. Seitz[7] and J. C. Slater[8] have calculated the energies and lattice constants of sodium and lithium on the basis of free electron binding.

With the adamantine class and the B-group metals, it is impossible to go so far. Clearly, here a considerable part of the lattice energy is derived from the degree of filling of the Brillouin

[3] *Z. Physik*, 1933, **80**, 763.

[4] *Proc. Roy. Soc.*, 1934, [*A*], **147**, 396; *A.*, 1935, 153.

[5] *Z. Physik*, 1935, **94**, 231; *Metallwirt.*, 1935, **14**, 145.

[6] "The Solid State of Matter," *Phys. Soc. Rep.*, 1935, p. 36.

[7] *Physical Rev.*, 1933, **43**, 804; 1934, **46**, 509, 1102; 1935, **47**, 400.

[8] *Ibid.*, 1934, **45**, 794; *Rev. Mod. Physics*, 1934, **6**, 209.

zones as in the Jones theory. The corresponding calculations have been done for the diamond[9] with qualitatively satisfactory results, although no theory has as yet served to explain the very remarkable optical and photoelectric properties of diamonds which, as (Sir) R. Robertson, J. J. Fox, and A. E. Martin[10] have shown, differentiate them into two widely different types.

The adamantine compounds can, however, also be formulated as macro-molecules with shared electron orbitals. They mark the boundary between the explanation of crystal structures by metallic or by homopolar conceptions.

The structure of the transition metals offers more theoretical difficulties because here the core as well as the free electrons has to be taken into account. K. Fuchs[11] has calculated the equilibrium copper lattice with fair success.

The magnetic and electrical properties of the transition metals and of some of their alloys, particularly those of nickel, have been discussed from a somewhat different point of view by N. F. Mott.[12] In the case of the transition metals partially filled *d* levels exist, and the extra electrons contributed by other atoms in the alloy can go to fill up these levels. U. Dehlinger[13] from structure considerations concludes that all the transition metals except iron contain only one *s* electron. We are, however, far from having as yet an adequate theory of the transition metals.

Order–Disorder Transformations in Alloys.—Where two metals are alloyed together, a series of solid phases is in general formed. The composition of each phase can be varied continuously over a certain range, within which the alloy remains homogeneous, and which generally includes a composition of relatively simple atomic proportions. We may therefore regard each phase as having some ideal composition, departures from which can take place without the appearance of a new phase by the statistical replacement of some atoms of one constituent by atoms of the other. Thus, to take a concrete example, in the system Au–Cu two of the phases have the ideal compositions CuAu and Cu_3Au. When we investigate the structure of such a phase, we find in general that in a properly annealed specimen the two types of atom assume definite relative positions in the structure. In the phase Cu_3Au, the gold atoms are found at the corners of a simple cubic unit cell, the copper atoms occupying the centres of the faces. Such a structure is termed a

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[9] W. F. Laschkarev and A. S. Tschabau, *Physikal. Z. Sovietunion*, 1935, **8**, 240; Kimball, *J. Chem. Physics*, 1935, **3**, 560; Nath, *Proc. Indian Acad. Sci.*, 1934, **1**, [*A*], 333; 1935, **1**, [*A*], 841; **2**, [*A*], 143.

[10] *Phil. Trans.*, 1934, [*A*], **232**, 463.

[11] *Proc. Roy. Soc.*, 1935, [*A*], **151**, 585.

[12] *Proc. Physical Soc.*, 1935, **47**, 571.

[13] *Z. Physik*, 1935, **96**, 620.

'super-lattice.' If, however, the alloy is not annealed but quenched from a sufficiently high temperature, we find that, while precisely the same sites are occupied by atoms as in the super-lattice, the distribution of the two metals between them is no longer regular but purely random. Thus, in the example we have quoted, the structure becomes essentially a face-centred cubic one, with a unit cell of the same size as before, but in which each site is occupied by ($\frac{3}{4}$Cu + $\frac{1}{4}$Au).

The transition between the ordered distribution in the super-lattice and the corresponding disordered arrangement has been the subject of much recent work.[14] All the authors agree in treating it essentially as a problem of dynamic equilibrium in which the atoms seek to take up the ordered arrangement of lowest potential energy, while thermal agitation seeks to promote a state of disorder. Here we shall follow in the main the discussion of W. L. Bragg and E. J. Williams, for although it cannot claim to be the earliest treatment of the order–disorder transformation, yet it contains many novel features and has the additional advantage of being mathematically less formal than that of the other authors, and therefore, perhaps, more suitable for this Report.

Consider a structure in a condition intermediate between the extreme ordered and disordered states. Its state may be represented by a quantity S, the degree of order, whose value is unity for the ordered arrangement of the super-lattice and zero for the state of complete disorder. (The exact definition of S is irrelevant for our discussion, and in fact, the quantity is differently defined by the several authors.) For a given value of S, and at a given temperature T, we may then define a quantity V as the increase in potential energy of the crystal when one atom is moved from an ordered to a disordered position. This quantity V is not a constant but a function of S, for when $S = 0$ the distinction between ordered and disordered positions vanishes and V must be zero; V will rise to a maximum value V_0 when $S = 1$. As a first approximation, V is assumed to be proportional to S and to vary only slowly with T. The general form of the variation of V as a function of S at several different temperatures is shown by the curves of Fig. 1*b*.

If, now, we consider the crystal at a temperature T', the condition that a degree of order S is one of dynamical equilibrium at that temperature leads to an expression for S as a function of V and T. Here we shall expect the form of the relation to be more exactly determined, for on the assumption of thermal equilibrium, the distribution of atoms as between the ordered and the disordered position will be given by the Boltzmann relation as a function of V/kT. Without entering into details, we may say that Bragg and Williams show that the general form of the relation will be that shown by the curves of Fig. 1*a*. At low temperatures, or for large values of V, the degree of order approaches unity, while for small values of V or under conditions of extreme thermal agitation, the degree of order is very small. The equilibrium degree of order at any temperature T is given by the intersection of the two corresponding curves of Fig. 1. At high temperatures the only intersection is at 0, corresponding to complete disorder. At low temperatures it is easy to see that the intersection at 0 corresponds to an unstable equilibrium, and that a second intersection at a finite value of S represents the stable equilibrium. This value of S tends to unity as T approaches zero. This second intersection will only occur below a certain critical temperature T_c, and from the nature of the curves it is clear that the point of intersection varies very rapidly as T falls below this critical temperature. On cooling, there is therefore a sudden onset of order below T_c, followed by a more gradual increase towards unity.

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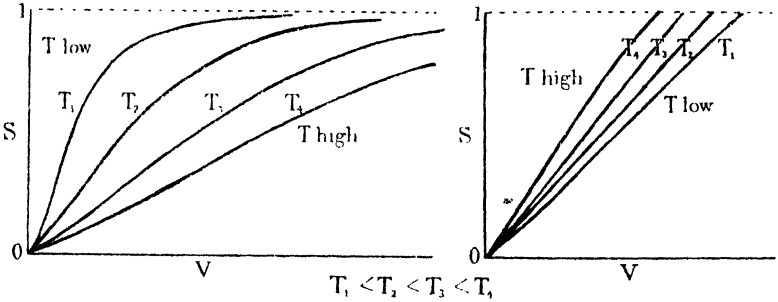
[14] W. Gorsky, *Z. Physik*, 1928, **50**, 64; U. Dehlinger, *ibid.*, 1933, **83**, 832, and earlier papers; *Z. physikal. Chem.*, 1934, [*B*], **26**, 343; *A.*, 1934, 724; G. Borelius, *Ann. Physik*, 1934, **20**, 57, 650; *A.*, 1934, 724; 1935, **24**, 489; W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.*, 1934, [*A*], **145**, 699; *A.*, 1934, 954; 1935, [*A*], **151**, 540; H. A. Bethe, *ibid.*, **150**, 552; *A.*, 1193; W. Hume-Rothery and H. M. Powell, *Z. Krist.*, 1935, **91**, 23.

FIG. 1.



(*a*) (*b*)

Formally, the theory of order–disorder is closely analogous to that of ferromagnetism, the ordered form corresponding to the ferromagnetic, and the disordered to the paramagnetic state; T_c corresponds to the Curie point.

The existence of this critical temperature is the most important feature of the theory, for it is to be expected that at this temperature many of the physical properties of the alloy will display sharp changes. In particular, anomalies in the specific heat will be expected, for as the temperature of the alloy is raised, extra thermal energy must be supplied to break down the ordered structure of the crystal. The specific heat will, therefore, rise gradually to the critical temperature and then, all order being destroyed, fall abruptly to its normal value. Bethe, who discusses the question of specific heats in rather more detail, shows that, although the order as defined by Bragg and Williams disappears at the temperature T_c, there is still a measure of 'local order' which persists above this temperature and contributes to the energy of the structure. Above T_c, therefore, the specific heat of the alloy is still somewhat larger than its normal value. In this form, the theory is in very satisfactory agreement with the specific-heat measurements of C. Sykes[15] on the alloy CuZn.

A somewhat different type of transformation between the ordered and disordered states takes place when the curves of Fig. 1*a* have a point of inflexion, being curved to the x axis in the neighbourhood of the origin. This will be the case, as Bragg and Williams show, for the alloy Al_3Au. Now, there will no longer be a continuous, albeit rapid, decrease of S as the temperature reaches T_c, for there will be a certain temperature at which the curve of Fig. 1*b* will be tangential to that of Fig. 1*a*, not at the origin but at some point corresponding to a finite value of S. Above this temperature, the curves will not intersect at all and the degree of order will fall abruptly to zero. In this case, the energy change associated with the transformation must be regarded as a latent heat of transformation rather than as an anomalously high specific heat. Here again, the theory is in satisfactory agreement with Sykes's measurements on Cu_3Au.

In both cases the development of the ordered from the disordered phase is a process which depends on the rate of cooling. At any given temperature below T_c there is a definite rate at which the order increases. Bragg and Williams have shown that a time of relaxation τ exists, after which the departure from equilibrium reaches $1/e$ of its original value T, and which is given by $e^{-\log A(T_1/T-1)}$, where $A = 10^{-12}$ sec. and T_1 is the temperature for which the time of relaxation is 1 sec. If T/T_1 is $\frac{1}{2}$, τ is 30,000 years, so that the alloy will never in practice reach order at temperatures less than $\frac{1}{2}T_1$. This fixes another characteristic temperature, the importance of which is that no ordered state for which $T_c < \frac{1}{2}T_1$ can ever be formed by cooling. This is the probable reason why superstructures other than very simple ones do not appear.

The theory of order and disorder in crystal structures has been studied chiefly in metals, but analogous phenomena are being observed with increasing frequency with other compounds, particularly among mixed oxides, sulphides, and halides. The interstitial and subtraction "Berthollide" compounds[16] have, in general, atoms which occupy a larger number of lattice points, either regularly (ordered) or statistically (disordered). These compounds have been discussed by E. J. W. Verwey[17] and G. Hägg.[18] Of particular interest is the compound Ag_2HgI_4 which exists[19] in two forms—a tetragonal form with definite positions of the metal atoms, and a higher-temperature cubic form in which the metal atoms occupy statistically three out of the four octahedral positions. A more extreme case is provided by the high-temperature form of silver iodide,[20] where the silver atoms occupy one of the three possible octahedral holes of the body-centred iodine lattice.

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[15] *Proc. Roy. Soc.*, 1935, [*A*], **148**, 422.

Further examples of this phenomenon are $(Li^{I}Ti^{4+})O$[21] with an NaCl lattice, $Ce_{2/3}WO_4$[22] isomorphous with $CaWO_4$, the tungsten bronzes Na_xWO_3,[23] in which the WO_3 lattice takes up Na atoms by lowering the tungsten valency, and the heteropoly-acids.[24]

This phenomenon is closely related to the polysynthetic twinning which is being found very frequently in layer and chain lattices. Cadmium bromide,[25] for instance, occurs in a cell containing one-third of a molecule due to existence of alternate layers of $CdCl_2$ and CdI_2 structures. $Pd(NH_3)_2Cl_2$,[26] AgCN,[27] and cristobalite[28] show analogous two-dimensional lattices. Disordered and statistical phenomena in crystals are, indeed, generally to be expected whenever different structural arrangements exist having approximately the same energy.

Formally analogous to the order–disorder phenomenon is that of the rotation of molecules in crystals.[29] The general theory has now been given by R. H. Fowler.[30] Two kinds of change occur, in general. In the first, the inception of rotation coincides with a change of crystal structure and there is a definite latent heat.

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[16] See *Ann. Reports*, 1933, **30**, 381.

[17] *J. Chem. Physics*, 1935, **3**, 592.

[18] *Z. Krist.*, 1935, **91**, 114.

[19] J. A. A. Ketelaar, *ibid.*, 1934, **87**, 436; *A.*, 1934, 947; *Z. physikal. Chem.*, 1934, [*B*], **26**, 327; 1935, **30**, 53.

[20] L. W. Strock, *Z. physikal. Chem.*, 1934, [*B*], **25**, 441; *A.*, 1934, 834.

[21] E. Kordes, *Z. Krist.*, 1935, **91**, 193; **92**, 139.

[22] J. Beintema, *Proc. K. Akad. Wetensch. Amsterdam*, 1935, **38**, 1011.

[23] G. Hägg, *Z. physikal. Chem.*, 1935, [*B*], **29**, 192; *Nature*, 1935, **135**, 874.

[24] See ref. (97), p. 220.

[25] See ref. (94), p. 209.

[26] F. G. Mann, (Miss) D. Crowfoot, D. C. Gattiker, and (Mrs.) N. Wooster, *J.*, 1935, 1642.

[27] C. D. West, *Z. Krist.*, 1935, **90**, 555; *A.*, 1194; 1934, **88**, 173.

[28] W. Nieuwenkamp, *ibid.*, 1935, **90**, 377.

[29] See *Ann. Reports*, 1931, **28**, 290.

[30] *Proc. Roy. Soc.*, 1935, [*A*], **151**, 1; *A.*, 1197.

In the second, the inception of rotation is gradual, but it becomes complete at a definite temperature : there is no latent heat but an anomalous rise in the specific heat. In general, these first and second types of change occur in different substances, but B. Ruhemann has shown that both occur in ammonium chloride, the first at high the second at low pressures. L. Landau [31] has given the theory of this change-over, and has shown that a critical pressure must exist at which the two types coincide. The theory cannot be given here, but it expresses the fact that an increase of interaction between the movable parts beyond a certain degree causes all to move when one does, and therefore a change from the second to the first type of transformation. J. D. B.

The Properties of Real Crystals.

The mechanical properties of real crystals, in so far as they depart from those to be expected in a crystal having an ideal structure, were discussed in the last Report on Crystallography. During the period under review, however, the nature of the real crystal has been the subject of so many publications that no excuse is offered for once again discussing this subject. Apart from individual papers, two especially important publications may be mentioned: *viz.*, the Report of the International Conference on Physics on the Solid State of Matter [1] and an issue of the *Zeitschrift für Kristallographie* [2] devoted entirely to the real crystal.

Secondary Structure.—The conception of a crystal as having a block-like structure was originally advanced to explain the fact that the observed *X*-ray reflexions from a crystal are very much more intense and extend over a much wider angle than is to be expected from an ideal structure. This conception has since been applied in an attempt to explain many other ‘ structure-sensitive ’ properties, notably breaking strength, which cannot be satisfactorily accounted for in terms of the ideal lattice. The exact nature of this secondary structure, and even its very existence, is still, however, the subject of violent controversy. Thus, while many results are interpreted in terms of such a structure, and others [3] are alleged to give direct proof of its existence, other authors [4] have marshalled many facts which they claim render such a structure impossible, and at the same time criticise the evidence on which the secondary structure is based. Among the principal objections to a mosaic structure of the type postulated by Zwicky are: (1) The fact that coherent crystals can be grown as thin plates or hairs with linear dimensions less than those of the mosaic blocks. (2) The internal perfection of crystals which makes their use in optical systems possible. (3) Intersecting glide planes. Gliding is supposed to take place on so-called π-planes: gliding on two intersecting π-planes could only occur if the glide distance was an exact multiple of the π-plane spacing. (4) Crystal strength. The very low strength of crystals, compared with the value calculated from the ideal structure, does not require any secondary structure and can be explained as due to a tearing of the crystal starting from surface cracks.[5] A. Joffé[6] has shown that under appropriate conditions strength approximating to the theoretical can be achieved, while with glass, where there is no question of mosaic structure, the abnormally low strength observed can be attributed to tearing. Mica stretched in such a way that the edges remain stressless increases in strength ten times. (5) The energetics of the problem.[7]

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[31] *Physikal. Z. Sovietunion*, 1935, **8**, 113.

[1] The Physical Society, London, 1935; hereafter referred to as *Phys. Soc. Rep.*

[2] 1934, **89**, 193—415.

[3] F. Bitter, *Physical Rev.*, 1932, **40**, 125; *A.*, 1933, 1234.

[4] H. E. Buckley, *Z. Krist.*, 1934, **89**, 221, 410; *A.*, 1935, 150; M. J. Buerger, *ibid.*, p. 242.

A number of interesting observations have been explained by A. Goetz[8] in terms of a 'group' structure, but here again there are many objections.[9]

Another type of secondary structure, which seems to be less open to criticism, is the 'lineage structure' of M. J. Buerger.[10] Here all crystals are regarded as essentially filled in dendritic frameworks. The lack of perfect parallelism between lineages accounts for the observed decrease in X-ray extinction, but the structure is essentially not a mosaic one. It is only accurate to apply the term mosaic to one cross section of the crystal, for in three dimensions the mosaic 'blocks' join one and the same parent stock at the original crystal nucleus. The 'blocks' are lineages just as are the branches of a dendrite. Buerger supports his views by a number of beautiful photographs, and is able to account in a general way for most of the structure-sensitive properties normally explained in terms of a secondary structure. In this connection we may refer the reader to the work of A. Papapetrou[11] on the growth of dendritic crystals.

On the experimental side, the extreme difficulty of obtaining reproducible results, and the amazing discrepancies between the observations of different schools, make it difficult to establish any unquestionable conclusions. To instance only one example, all authors are agreed that wetting a rock salt crystal has a profound effect on its plastic properties and breaking strength. K. Wendenburg [12] argues that the effect is a volume one due to penetration of the water into the crystal, since the effect persists if the surface is subsequently dried. Absorption spectra are also said to reveal the presence of water in the crystal. A. Joffé,[13] however, claims that the effect cannot be a volume one since the strength of a wetted crystal, one region on the surface of which is protected by vaselin, is that of a dry crystal. If water entered the volume of the crystal it would penetrate to all parts in spite of the vaselin.

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[5] E. Orowan, *Phys. Soc. Rep.*, p. 81; *Z. Krist.*, 1934, **89**, 327; *A.*, 1935, 151.

[6] *Phys. Soc. Rep.*, p. 77.

[7] M. J. Buerger, *Z. Krist.*, 1934, **89**, 242; E. Orowan, *Phys. Soc. Rep.*, p. 81.

[8] *Z. Krist.*, 1934, **89**, 310; *A.*, 1935, 151; *Phys. Soc. Rep.*, p. 62.

[9] H. E. Buckley, *Z. Krist.*, 1934, **89**, 221; *A.*, 1935, 150.

[10] *Ibid.*, p. 195.

[11] *Ibid.*, 1935, **92**, 89.

That a secondary structure is not an essential characteristic of crystal is indicated by the fact that crystals of rock salt can be prepared [14] which give the X-ray reflexion deduced from the ideal lattice. A summary of existing theories of real crystals is given by A. Smekal.[15]

Plasticity.—Closely allied to the question of secondary structure is that of the plastic properties of single crystals. In the "Distortion of Metal Crystals" [16] and elsewhere,[17] accounts are available of the many observations on plastic deformation. The essential features which any theory of plasticity must explain are : (1) Plastic distortion sets in when the shear stress reaches a certain critical but very small value. (2) The distortion may take place either by gliding along definite crystallographic planes in definite directions, or by twinning. (3) The occurrence of plastic deformation is always accompanied by a 'hardening' or increase in the stress required to produce further deformation. In this connexion, it is important to realise, as A. W. Stepanow [18] has pointed out, that breaking strength and plasticity are in no way related, and that no increase in breaking strength takes place on plastic deformation. The anomalously low breaking strength, as we have seen, is to find its explanation in the secondary structure : it can only be measured under conditions in which plastic flow is prevented.

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[12] *Z. Krist.*, 1934, **88**, 727; *A.*, 1934, 721.

[13] *Phys. Soc. Rep.*, p. 72; see also E. W. Zehnowitzer, *Nature*, 1935, **135**, 1076; *A.*, 956.

[14] M. Renniger, *Naturwiss.*, 1934, **22**, 334; *A.*, 1934, 720; *Z. Krist.*, 1934, **89**, 344; *A.*, 1935, 151; P. P. Ewald and M. Renniger, *Phys. Soc. Rep.*, p. 57.

[15] *Z. Krist.*, 1934, **89**, 386; *A.*, 1935, 151.

[16] (Miss) C. F. Elam (Oxford, Clarendon Press, 1935).

[17] W. G. Burgers, *Phys. Soc. Rep.*, p. 139; E. Schmid, *ibid.*, p. 161; W. G. Burgers and J. M. Burgers, First Report on Viscosity and Plasticity, *Verh. K. Akad. Amsterdam*, 1935, **15**, 173.

[18] *Z. Physik*, 1934, **94**, 42.

The same author[19] has suggested that plasticity may be accounted for in terms of the intense local heating developed in the neighbourhood of the glide planes, which produces a temporary dissociation of the lattice. That such a mechanism is not impossible is indicated by the experiments of F. P. Bowden and K. E. W. Ridler,[20] who found that the surface temperature of sliding metals may reach very high values although the bulk of the metal remains at room temperatures. High temperatures produced by plastic deformation may play an important part in detonation.[21] The great plasticity of silver chloride compared with that of rock salt, which has the same structure and very nearly the same lattice dimensions and lattice energy, suggests that the difference may be due to the difference of polarisation properties of sodium and silver, which also accounts for the absence of cleavage in silver chloride.[22]

A more precise, mathematical theory of the plasticity of crystals has been developed by G. I. Taylor,[23] who pictures slip as taking place by the propagation of a ‘ dislocation ’ along the slip plane. Such a ‘ dislocation ’ may be pictured by considering a point P in the slip plane, such that some distance beyond P the lattice is continuous across this plane, while at some distance on the other side of P the lattice is again continuous but with the portion on one side of the slip plane displaced relative to that on the other through the length of the unit cell. In the immediate neighbourhood of P, the lattice is distorted, but where P has passed along the slip plane the ideal lattice is restored except that one half is displaced relative to the other. To bring about such a displacement by causing all the atoms in one plane to jump simultaneously through the length of one unit cell would require a force of the order of magnitude of the elastic modulus, but if the displacement occurs by the atoms in the neighbourhood of the dislocation jumping one by one, thereby propagating the dislocation, the force required is much smaller, since the field of force in the immediate neighbourhood of the dislocation is profoundly altered. Calculation shows, in fact, that under the influence of the smallest stress, thermal agitation alone should suffice to propagate the dislocation, so that an ideal lattice should be infinitely weak. Taylor overcomes this objection by supposing that, after travelling a distance L, the dislocation encounters one of the ‘ faults ’ of the secondary structure and then stops. In this way a parabolic relation is derived between the stress and the amount of plastic distortion, which is in good agreement with observations on rock salt and metal crystals. The experiments enable a value of L of about 10^{-4} cm. to be deduced, and this is of the correct order of magnitude for most of the theories of secondary structure.

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[19] *Z. Physik*, 1933, **81**, 560.

[20] *Proc. Camb. Phil. Soc.*, 1935, **31**, 431.

[21] A. Michel-Lévy and H. Muraour, *Compt. rend.*, 1934, **198**, 1499; *A.*, 1934, 605.

[22] A. W. Stepanow, *Physikal. Z. Sovietunion*, 1934, **6**, 312; 1935, **8**, 25.

[23] *Proc. Roy. Soc.*, 1934, [*A*], **145**, 362, 387; *A.*, 1934, 950; *Z. Krist.*, 1934, **89**, 375; *A.*, 1935, 151.

Another picture of the mechanism of plastic deformation, due to E. Orowan,[24] regards it as essentially a dynamic phenomenon. Consider a crystal under the influence of a shearing stress τ_a, itself insufficient to cause gliding. Under the influence of local thermal fluctuations, the stress will occasionally reach a value exceeding some critical value τ_R and local slip will take place. This is most likely to happen at places where the stress is already concentrated owing to material inhomogeneities, so that we must replace the mean stress τ_a by $q\tau_a$, where q is a factor expressing the local concentration of stress. The increase of stress from $q\tau_a$ to τ_R corresponds to an increase of elastic energy proportional to $(\tau_R - q\tau_a)^2$, and it is therefore assumed that the probability of such an occurrence is given by the Boltzman equation $W = \text{const.} \times e^{-(\tau_R - q\tau_a)^2/kT}$. The velocity of the deformation process is evidently proportional to this probability. In this form, the theory gives a finite rate of deformation for all values of the applied stress. The exponential factor, however, results in such a rapid increase in velocity with applied stress that there will be some critical stress below which the velocity is too small to be observed, as is found to be the case experimentally. Orowan's theory gives a satisfactory account of the parabolic relationship between stress and amount of deformation, and also of the observed temperature variation of critical stress. A suggested combination of the theories of Taylor and Orowan has been advanced by Burgers and Burgers.[25] J. D. B.

CRYSTALLOGRAPHY.

The Technique of Structure Analysis.—The field of X-ray structure analysis has enjoyed two important additions to its bibliography during the period under review. "International Tables for Crystal Structure Determination"[1] is the outcome of the work of an international committee of crystallographers set up 1929,[2] and contains a wealth of information for those engaged on structure analysis. The first volume comprises diagrams of the equivalent general position in the 230 space groups, together with the structure factors and a list of the characteristic reflexions both for the general and for special positions in each space group. The second volume contains tables of many trigonometrical functions and physical quantities frequently required in structural analysis, as well as an account of graphical methods of interpreting *X*-ray photographs. "*X*-Rays in Theory and Experiment,"[3] a second and greatly enlarged edition of "*X*-Rays and Electrons," contains some 150 pages devoted to a very full account of the theory of the diffraction of *X*-rays by a crystal grating, much of which was previously unavailable in the English language outside original papers.

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[24] *Z. Physik*, 1934, **89**, 605, 614, 634; 1935, **97**, 573.

[25] *Op. cit.*, ref. (17).

[1] Bell, 1935 (two vols.).

[2] See *Ann. Reports*, 1931, **28**, 263.

The experimental methods of structure analysis have suffered no fundamental changes in the last two years. Two papers,[4] dealing with the Weissenberg camera and with the interpretation of the photographs obtained, reflect the increasing use which is being made of this instrument. Photographic methods of intensity measurement have now become a common practice. In a moving-film camera described by J. M. Robertson,[5] the crystal under investigation and a standard crystal are alternately exposed to the *X*-ray beam so that a number of reflexions of known intensity are present on the film: by comparison with these reflexions, unknown intensities can be determined with an accuracy amply sufficient for structure analysis in a fraction of the time required for ionisation-spectrometer measurements. The method, moreover, is available for many substances which will not form crystals sufficiently large for use on the ionisation spectrometer. Conditions necessary for making accurate intensity measurements on powder photographs have been discussed by G. W. Brindley and F. W. Spiers,[6] by J. C. M. Brentano,[7] and by B. W. Robinson.[7a] Precise measurements of lattice constants and the geometrical and other errors which arise in such measurements are reviewed by several authors.[8] Various methods have been suggested[9] for reducing the exposure times required for powder photographs. New forms of camera suitable for use at low temperatures or where the crystal must be kept in a vacuum have been described by E. Pohland[10] and by B. Ruhemann.[11]

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[3] A. H. Compton and S. K. Allison (Macmillan, London, 1935).

[4] M. J. Buerger, *Z. Krist.*, 1934, **88**, 356; (Miss) D. M. Crowfoot, *ibid.*, 1935, **90**, 215.

[5] *Phil. Mag.*, 1934, **18**, 729.

[6] *Proc. Physical Soc.*, 1934, **46**,, 841.

[7] *Ibid.*, 1935, **47**, 932; *A.*, 1306.

[7a] *Proc. Roy. Soc.*, 1934, [*A*], **147**, 467.

[8] M. U. Cohen, *Rev. Sci. Instr.*, 1935, **6**, 68; J. Köppel, *J. Phys. Radium*, 1934, **5**, 145; *A.*, 1934, 587; E. R. Jette and F. Foote, *J. Chem. Physics*, 1935, **3**, 605.

[9] W. E. Schmid, *Z. physikal. Chem.*, 1933, [*B*], **23**, 347; *A.*, 1934, 162; J. P. Blewett, *J. Sci. Instr.*, 1934, **11**, 148; *A.*, 1934, 624; A. Rogozinski, *Compt. rend.*, 1934, **198**, 953; *A.*, 1934, 503.

[10] *Z. physikal. Chem.*, 1934, [*B*], **26**, 238; *A.*, 1934, 985.

[11] *Physikal. Z. Sovietunion*, 1935, **7**, 572.

The great power of X-ray methods, and especially of the powder method, in attacking many problems of a more general character than those involved in pure structure analysis, is at last being recognised. Such varied problems as a qualitative and even quantitative chemical analysis of material of which only minute quantities are available, the determination of grain size in metals and other crystalline substances, and the detection of strain in castings, have all been successfully attacked by X-ray methods. An investigation[12] into the constitution of bleaching powder was largely carried out by these methods, while W. P. Jesse[13] has described quantitative analyses of metal systems accurate to 1%. A special number of the *Kolloid Zeitschrift* (1935, **69**, Heft 3) is devoted to X-ray and electron methods in colloid science, while a popular account of such applications of X-ray analysis, especially in the industrial field, has been published.[14] Yet it is true to say that there are many investigations to which these methods are particularly suited which are still being attacked by older and less satisfactory means.

One important contribution has appeared during the period under review which promises to be of considerable value in the elucidation of complex structures. The representation of the electron density throughout a structure, as projected on any plane in the structure, by means of a Fourier synthesis affords an elegant means of presenting the results of a structure analysis. It is not, however, of great value in determining an unknown structure, for although intensity measurements give us the magnitudes of all the terms of the Fourier synthesis, they can tell us nothing of the signs. These signs can only be determined when the positions of most of the atoms in the structure have been found by other experiments. A. L. Patterson[15] has shown that, if we form the Fourier synthesis, using not the amplitudes but the intensities of the X-ray reflexions as the coefficients of the corresponding terms in the synthesis, the resultant plot is such that the vectors joining the origin to each of the several peaks represent in length and direction, but not, of course, in position, interatomic distances in the structure. In Fig. 2*a* an example of such a plot is given for hexachlorobenzene. This substance is monoclinic, and the plane of the benzene ring is nearly parallel to the (010) face. Fig. 2*b* shows a projection of the molecule on this face, and all the prominent peaks in Fig. 2*a* may be readily associated with the corresponding interatomic distances in the molecule. The distances in Fig. 2*b* give rise to the peaks in Fig. 2*a* bearing the same letters. In more complex structures, the number of interatom distances will be so large that only the most prominent between the heaviest atoms will be expected to stand out in a Patterson synthesis, and to this extent the method has its limitations and perhaps gives little more information than would be deduced from general considerations by an experienced worker in

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[12] C. W. Bunn and others, *Proc. Roy. Soc.*, 1935, [*A*], **151**, 141 (see this vol., p. 158).

[13] *Rev. Sci. Instr.*, 1935, **6**, 47; *A.*, 1934, 446.

[14] "Industrial Application of X-Ray Crystal Analysis," H.M. Stationery Office, 1934.

[15] *Physical Rev.*, 1934, **46**, 372; *A.*, 1934, 1160; *Z. Krist.*, 1935, **90**, 517, 543; *A.*, 1193.

FIG. 2*a*.

Hexachlorobenzene. Contour map of the $F^2(h0l)$ *series.*

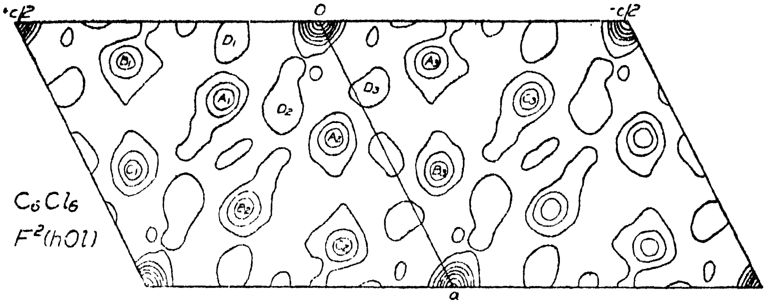
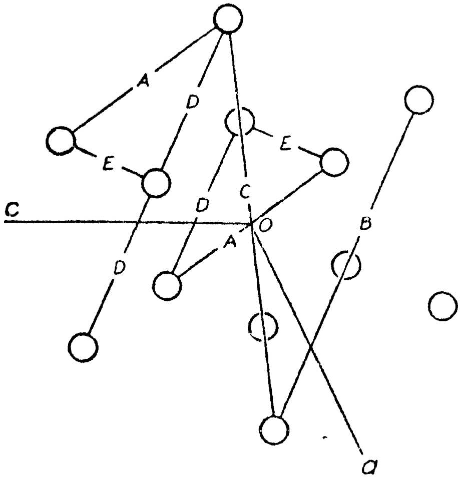


FIG. 2*b*.

Interatomic distance diagram for the C_6Cl_6 *molecule. The inner ring consists of carbon atoms, the outer of chlorines. The interatomic distances indicated are repeated six times in approximate hexagonal symmetry. The molecule is actually centrosymmetrical. The distances in this diagram give rise to the peaks in Fig.* 2a *bearing the same letters.*



structural analysis. At the same time, the Patterson synthesis does afford the only means of giving an unprejudiced presentation of all the information which may be directly derived from the experimental material. The method has already been applied to a determination of the structure of nickel sulphate heptahydrate[16] where it threw considerable light on the position of the nickel and the sulphur atoms.

The tedious calculations involved in the formation of a Fourier synthesis may be considerably lightened by the methods of C. A. Beevers and H. Lipson[17] and J. M. Robertson.[18] R. C. E.

CRYSTAL CHEMISTRY.

There have been no notable advances in general crystal chemistry in the past two years. The general picture elaborated by Bragg, Goldschmidt, and Pauling still continues to hold the field. L. Pauling and M. L. Huggins[1] have, however, extended their work on atomic dimensions to include covalent binding. In an important paper they discuss the theory of the covalent link on the basis of the directed bond picture. This enables them to predict the magnetic moments to be associated with the four types of bonds discussed, *viz.*, the tetrahedral bonds sp^3, the square bonds dsp^2, the octahedral bonds d^2sp^3, and the 8-co-ordinate bonds d^4sp^3. In this way they are able to distinguish between ionic and covalent bonding in complexes. For instance, they show that the FeF_6 complex is essentially one of ionic bonds, whereas $Fe(CN)_6$ has covalent bonds. In a semiempirical way they construct tables which give an effective radius for the tetrahedral, square, and octahedral and trigonal prism radii. These tables are given below.

Standard Tetrahedral Radii.

	Be.	B.	C.	N.	O.	F.
	1·07	0·89	0·77	0·70	0·66	0·64
	Mg.	Al.	Si.	P.	S.	Cl.
	1·40	1·26	1·17	1·10	1·04	0·99
Cu.	Zn.	Ga.	Ge.	As.	Se.	Br.
1·35	1·31	1·26	1·22	1·18	1·14	1·11
Ag.	Cd.	In.	Sn.	Sb.	Te.	I.
1·53	1·48	1·44	1·40	1·36	1·32	1·28
	Au.	Hg.	Tl.	Pb.	Bi.	
	1·50	1·48	1·47	1·46	1·46	

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[16] C. A. Beevers and C. M. Schwartz, *Z. Krist.*, 1935, **91**, 157.

[17] *Phil. Mag.*, 1934, **17**, 855.

[18] *Ibid.*, 1936, **21**, 176.

[1] *Z. Krist.*, 1934, **87**, 205; *A.*, 1934, 350.

Standard Octahedral Radii (from Pyrite-type Crystals).

Valency.	Fe.	Co.	Ni.	Ru Os	Rh Ir	Pd Pt	Ag Au
II …………	1·23	1·32	1·39	1·33	1·43	1·50	1·54 *
III …………		1·22	1·31		1·32	1·42	1·49
IV …………			1·21			1·31	1·41

* Obtained by extrapolation.

Square Radii.

Co^{I}.	Ni^{II}.	Cu^{III}.	Rh^{I}. Ir^{I}.	Pd^{II}. Pt^{II}.	Ag^{III}. Au^{III}.
1·23	1·22	1·21	1·33	1·32	1·31

Trigonal prism radii : Mo, 1·37; W, 1·44.

These radii would be better called half-bond lengths, as the covalencies are definitely directed, and the radii of the atoms, other than covalent bonds, may be as much as twice as large.

H. G. Grimm [2] has made a general survey of chemical compounds of the type A_mB_n. He has discussed the conditions which determine their general character—metallic, adamantine, ionic, and molecular—and has produced a table showing the known type of compounds formed between every pair of elements in the periodic table.

R. C. Evans, in translating O. Hassel's "Crystal Chemistry" (London, Heinemann), has made available in English a simple and attractively written account of the subject, but one which unavoidably does not include much recent work. R. W. G. Wyckoff has produced an extremely valuable supplement to the second edition of "The Structure of Crystals," which gives references and beautifully drawn diagrams to all of the important crystal structures determined in the years 1930—1934. Pending the second edition of the "Strukturbericht," this is a most valuable compilation for chemists and crystallographers, particularly because every structure is critically examined and those described may be considered to be well established.

Metallic Structures.—Our knowledge of the electronic theory of metals, discussed earlier in this Report, has been of great assistance in understanding the crystal structure of metals and alloys, and has, in general, justified the empirical classification put forward in previous reports. Three main factors are found to influence these structures : the sizes of the atoms, the number of electrons per atom in the phase as a whole, and the heterogeneity of the atoms composing the alloy.

Most of the alloy structures investigated earlier had atoms of approximately the same size, and consequently this factor did not enter into consideration. The three types of alloy distinguished were those in which the atoms were of the same electronic type, which gave rise to unbroken solid solutions, such as the system gold–silver; those in which the atoms had a different number of electrons, and consequently where the average number of electrons per atom varied with the concentration—these are the substances whose structures obey the Hume-Rothery rules now explained by Jones—and finally, alloys where the difference of the number of electrons is very great, sometimes tending to pass over into semi-metals. The sequence, as given by U. Dehlinger[3] in a general review of metallic mixed crystals and compounds, is as follows: Mixed crystals, super-structures, inter-metallic compounds, corresponding to increasing affinity, a diminished region of homogeneity and an increasing difference in physical properties and crystal structure compared to the component metals. No hard and fast lines can be drawn between these different types of combination, and this gives metal chemistry a particularly indefinite character.

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[2] *Angew. Chem.*, 1934, **47**, 53; *A.*, 1934, 234.

The rôle of differences in atomic size is beginning to be apparent. Two compounds have been known for some time, *viz.*, Cu_2Mg and Zn_2Mg, which may be described as close-packed structures of copper or zinc respectively with cubic and hexagonal close-packed lattices in which a large magnesium atom is inserted in the place of two copper or zinc atoms. These types are now found to have a far wider significance, and to occur, in fact, in nearly all cases where the radii of the atoms concerned are in a ratio of between 1 : 1·15 and 1 : 1·3, or a volume ratio of approximately 1 : 2. Thus, F. Laves and K. Löhberg[4] have pointed out that KBi_2, ZrW_2, $PbAu_2$, $CuBe_2$, and MgNiZn belong to the $MgCu_2$ type, while $MgNi_2$, MgCuAl, $FeBe_2$ belong to the $MgZn_2$ type. The occurrence in these lists of metals of a totally different chemical nature shows that the structures cannot be due to any electronic factors, but are simply the expression of the nearest approach to close-packing which can be made by atoms of widely different atomic volume. They may be regarded as substitution compounds or solid solutions in which one atom of one type replaces two of another and, as Laves has shown, such compounds are not confined to binary alloys. Thus the quaternary compound $Mg_3Zn_2Cu_2Ni_2$ belongs to the Cu_2Mg type. There are probably a limited number of other such compounds with different volume and atom ratios: thus Zn_5Mg and $FeBe_5$ possess modifications of the Zn_2Mg and the Cu_2Mg structure respectively. The simplest cases of all are where alloys are of the form AB, the structure of which is the well-known cæsium chloride type, while

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[3] *Angew. Chem.*, 1934, **47**, 621; *Z. Metallk.*, 1934, **26**, 227; *Z. Elektrochem.*, 1935, **41**, 344; cf. W. E. Schmidt, *Z. Metallk.*, 1935, **27**, 49.

[4] *Nach. Ges. Wiss. Göttingen*, 1934, **1**, 59.

Al_2Cu is an example of a type in which the small copper atoms are packed in the interstices of a deformed cubical close-packing of aluminium atoms. Further research will undoubtedly bring to light many more such compounds. They are likely to show a much more definite composition than those in which the atom sizes are more equal. But this is a purely geometrical fact, and does not depend on any greater chemical affinity between the elements composing them.

The existence of an intermetallic compound may be due to three reasons by no means mutually exclusive. In the first place, it may be due simply to the existence in some simple ratio of atoms of different kinds. Such compounds will range from the ordered close-packing discussed above to the definite structures due to atoms of unequal sizes. Secondly, it may be due simply to the average number of free electrons available per atom, but this is likely to have a determining effect on the structure only when the atomic sizes are approximately equal. Thirdly, it may depend on the existence of loosely held electrons in one atom and electron affinity in the other. This will lead to further definite compounds which are strictly not all of a metallic character, such as Mg_2Pb.

Modern methods of the exact measurement of lattice dimensions have made it possible to get a closer view of the nature of intermetallic solid solution. E. R. Jette,[5] in a study of available information, shows that solid solutions can be divided into three types, in all of which the lattice constants are less than, equal to, or greater than that expected from Vegard's law : $a = a_A F_A + a_B F_B$, where F denotes atomic fractions. A smaller lattice constant indicates the special attraction between unlike atoms, a larger one a special attraction between like atoms. The former is shown by the systems Ag–Pt, Ag–Pd, Cu–Ni, and Cr–Fe, the latter by Cu–Au, Cu–Pd, Cu–Ag....Ag–Cu, Fe–Cr, and with Au–Pt, Au–Pd, Mo–W, Pt–Ir, Pt–Rh, Sb–Bi, there is no sensible deviation from Vegard's rule. The negative and positive variations can be correlated very roughly with the slope of the liquidus curve tending to be convex for negative, and concave for positive deviations, as might be expected.

The use of high-precision determination of lattice constants will soon become the most reliable gauge of purity of a metallic element. E. R. Jette and F. Foote [6] have determined the lattice constants of specially pure Al, Ni, Ag, Au, Si, Fe, Mo, W, Mg, Zn, Cd, Sb, Bi, and Sn, with a general accuracy of 1—2 parts in 40,000. Similar, but less accurate, determinations of other elements have been carried out by E. Owen, L. Pickup, and I. O. Roberts[7] and M. C. Neuburger.[8]

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[5] *Amer. Inst. Min. Met. Eng.*, 560 E.

[6] *J. Chem. Physics*, **1935, 3, 605.**

New super-structures Au_3Mn and AuMn, face-centred and body-centred tetragonal respectively, have been found to be precipitated at low temperatures from the extended solid solution of manganese–gold.[9] The only compounds of the transition metals which show definitely novel structures are the related substances Fe_2W and Fe_7W_6, and the corresponding molybdenum compounds determined by H. Arnfelt and A. Westgren.[10] In these structures there seems a definite tendency for tungsten or molybdenum atoms to associate in groups of two or four.

The interstitial compounds have been further investigated without, however, any startling discovery. Further work has been done on the solubility of hydrogen in the transition metals,[11] and the essentially protonic nature of the solution confirmed. The structure of steel is now, thanks to X-ray work, fairly firmly established. G. Hägg[12] has finally shown, by careful measurement of lattice parameters, that the only martensite formed by quenching of austenite (face-centred γ-iron containing carbon) has a tetragonal structure which gradually approximates to cubic α-iron with decrease of carbon content. The rate of decomposition of the martensite is shown to depend primarily on the temperature, but it is appreciable even at 100°. An excellent popular account of our present knowledge of the structure of steels is given by K. van Horn.[13] A higher carbide of iron, Fe_2C, has been described.[14] The highest carbide of nickel so far found is Ni_3C,[15] which consists of a hexagonal close-packed nickel structure with statistically distributed carbon atoms.

A study of the system Fe–Cr–N[16] shows only, besides the known iron nitrides, two chromium nitrides, Cr_2N, hexagonal, and CrN, cubic face-centred; but in the Fe–Al–C system[17] a new phase Fe_3AlC_x is found, face-centred cubic, in contrast with the body-centred Fe_3Al. A certain solubility of carbon in platinum has been reported.[18] The complex structures of the carbides of chromium Cr_7C_3 and manganese Mn_7C_3 with 80 atoms in the cell have been worked out by A. Westgren.[19] They consist of carbon placed interstitially into a distorted metal framework. The silicides of the transition metals have also been studied, particularly by B. Borén.[20] Cr, Mn, Co, and Ni all form compounds of the type MSi, showing the FeSi structure. The isotropic Mn_3Si, also studied by F. Laves,[21] is interesting as a simple body-centred structure in which manganese and silicon atoms occupy all positions indiscriminately. In Co_2Si there is an arrangement of silicon chains similar to those existing in Cr_3C_2,[22] the Si–Si distance in the chains being 2·15 Å.[23]

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[7] *Z. Krist.*, 1935, **91**, 70.

[8] *Ibid.*, **92**, 313; 1936, **93**, 1.

[9] H. Bumm and U. Dehlinger, *Metallwirt.*, 1934, **13**, 23.

[10] *Jernk. Ann.*, 1935, 185.

[11] H. Mundt, *Ann. Physik*, 1934, [v], **19**, 721; *A.*, 1934, 590; D. P. Smith and G. J. Derge, *Trans. Electrochem. Soc.*, 1934, **66**, 25; *A.*, 1934, 1168; M. H. Hey, J., 1935, 1254; *A.*, 1322; J. Franck, *Nach. Ges. Wiss. Göttingen*, Math.-phys. Kl., 1933, 293; *A.*, 1934, 1168.

[12] *J. Iron Steel Inst.*, 1934, **11**, 439; cf. J. Šplíchal and F. Cabicar, *Coll. Czech. Chem. Comm.*, 1934, **6**, 251; *A.*, 1934, 953.

[13] *Metal Progress*, Aug. 1935.

[14] G. Hägg, *Z. Krist.*, 1934, **89**, 92.

[15] J. Schmidt, *Z. anorg. Chem.*, 1933–34, **216**, 85.

[16] S. Eriksson, *Jernk. Ann.*, 1934, 530.

[17] F. R. Morral, *J. Iron Steel Inst.*, Sept. 1934; *A.*, 1934, 1166.

Electron Compounds.—No full account of *X*-ray studies of this field is given, as it is covered by the Report on non-ferrous alloys (p. 165). Only references will be made to newly established crystal structures.

Now that the theoretical basis for Hume-Rothery's rules has been established (see above), special interest attaches to the study of solubility limits of the system copper–silver, and the B-group elements including gallium, germanium, and indium. [24] In all cases where large differences of atomic size do not occur, the equilibrium diagrams depend on electronic and not on atomic proportions as the theory demands. In the nickel–zinc system [25] the tetragonal phases β and γ correspond approximately to the β-brass and ε to the γ-brass type. Ferromagnetic Heusler alloys, Mn–Al–Cu, are found to belong essentially to the β-type, with a regular superstructure.[26] A. J. Bradley and J. W. Rodgers [27] have used an extremely ingenious method to differentiate the positions of the copper and manganese atoms. These are normally indistinguishable by *X*-rays, but by using iron, copper, and zinc *K* radiation, anomalies in the scattering power of the elements in relation to the position of their absorption edges enable the distinction to be made.

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[18] L. J. Collier, T. H. Harrison, and W. G. A. Taylor, *Trans. Faraday Soc.*, 1934, **30**, 581; *A.*, 1934, 987.

[19] *Jernk. Ann.*, 1935, 231.

[20] *Arkiv Kemi, Min. Geol.*, 1934, **11**, *A*, No. 10; *A.*, 482.

[21] *Z. Krist.*, 1935, **89**, 189.

[22] See *Ann. Reports*, 1933, **30**, 390.

[23] B. Borén, S. Ståhl, and A. Westgren, *Z. physikal. Chem.*, 1935, [*B*], **29**, 231; *A.*, 1194.

[24] W. Hume-Rothery, G. W. Mabbott, and K. M. C. Evans, *Phil. Trans.*, 1934, [*A*], **233**, 1; *A.*, 1934, 725.

[25] K. Tamaru and A. Osawa, *Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 13; *A.*, 1934, 482; *Sci. Rep. Tôhoku Imp. Univ.*, 1934, **23**, 794; V. Caglioti, *Atti Congr. naz. Chim.*, 1933, **4**, 431; *A.*, 1934, 1166.

[26] O. Heusler, *Z. Metallk.*, 1933, **25**, 274; *A.*, 1934, 357.

[27] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 340; *A.*, 1934, 590.

New β- and γ-phases have been found in the copper–gallium [28] and copper–indium [29] systems, but analogous compounds do not occur in the silver–indium system.[30] The γ-structure which occurs anomalously for CuHg has been confirmed.[31]

New compounds and new structures have been found in the Fe–Al system.[32] The compounds $FeAl_2$, Fe_2Al_5, and $FeAl_3$ are all highly complex; $FeAl_3$ has a monoclinic cell of dimensions 47·4, 15·4, 8·1 Å., containing 400 atoms.[33] The platinum–thallium system contains one compound PtTl with a new and unusual structure.[34] The purple compound $AuAl_2$ proved to have a simple fluorite type of structure,[35] which may have some relation to its unusual physical properties. The silicides of the B-group metals have been much studied;[36] one, $Cu_{15}Si_4$, has a cubic cell containing 76 atoms. Compounds where large differences of atomic size occur have also been studied;[37] in particular, L. Misch has studied the compounds of beryllium with copper, nickel, and iron :[38] CuBe and NiBe have the cæsium chloride structures, $CuBe_2$ and $NiBe_5$ are of the $MgCu_2$ type, and $FeBe_2$ is of the $MgZn_2$ type; while Ni_5Be_{21} and Pt_5Be_{21} have a deformed γ-brass structure.

Alloys of A- and B-group metals. Our knowledge of the alloys of these metals has been considerably extended. U. Dehlinger [39] has made a useful survey of the known alloy structures and solid solutions of the elements Be, Mg, Zn, Cd, Hg, Al, and Sn. It appears quite definitely that the factors conducing to extended solid solution are similarities in electronic constitution rather than mere equivalence of atomic size. F. M. Jaeger and J. E. Zanstra [40] have made a detailed study of the allotropy of beryllium; the metastable form at 600° is orientated parallel to the original beryllium crystals and must be in some sense a super-lattice of dimensions $a = 7{\cdot}1$, $c = 10{\cdot}8$ Å. Such a lattice would contain about 60 atoms, and the exact determination of this structure would have great theoretical interest.

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[28] F. Weibke, *Z. anorg. Chem.*, 1934, **220**, 293.

[29] F. Weibke and H. Eggers, *ibid.*, p. 273.

[30] *Idem, ibid.*, 1935, **222**, 145; L. K. Frevel and E. Ott, *J. Amer. Chem. Soc.*, 1935, **57**, 228.

[31] F. Schoszberger, *Z. physikal. Chem.*, 1935, [*B*], **29**, 65.

[32] A. Osawa, *Sci. Rep. Tôhoku Imp. Univ.*, 1933, **22**, 803; *A.*, 1934, 137; *Kinz. no Kenk.*, 1933, **10**, 432; *A.*, 1935, 158.

[33] E. Bachmetew, *Z. Krist.*, 1934, **89**, 575.

[34] E. Zintl and A. Harder, *Z. Elektrochem.*, 1935, **41**, 767.

[35] C. D. West and A. W. Petersen, *Z. Krist.*, 1935, **88**, 93.

[36] E. R. Jette and E. B. Gebert, *J. Chem. Physics*, 1933, **1**, 753; *A.*, 1934, 137; F. R. Morral and A. Westgren, *Arkiv Kemi, Min. Geol.*, 1934, **11**, [*B*], No. 37; *A.*, 1934, 1165; K. Sautner, *Forschungsarb. Metallk. Röntgenmet.*, No. 9; *A.*, 1934, 482; S. Fagerberg and A. Westgren, *Metallwirt.*, 1935, **14**, 265.

[37] V. G. Sederman, *Phil. Mag.*, 1934, [vii], **18**, 343; *A.*, 1934, 953; H. Perlitz, *Kecmia Teated*, 1934, **2**, 11; *A.*, 1934, 1064; C. Dégard, *Z. Krist.*, 1935, **90**, 399; *A.*, 1198; T. Jurriaanse, *ibid.*, p. 323.

[38] *Z. physikal. Chem.*, 1935, [*B*], **29**, 42.

[39] *Z. Elektrochem.*, 1935, **41**, 20.

[40] *Proc. K. Akad. Wetensch. Amsterdam*, 1933, **36**, 636; F. M. Jaeger and E. Rosenbohm, *ibid.*, 1934, **37**, 67; *Rec. trav. chim.*, 1934, **53**, 451; *A.*, 1934, 589.

The alloys of lithium have been extensively studied, chiefly by G. Grube, E. Zintl, and their collaborators. In the Li–Mg system [41] there is no true compound formation, but the solid solution of composition $LiMg_5$ cannot take up any more magnesium, and functions towards it as a true compound. Apart from the compound LiZn,[42] with the NaTl structure, another compound Li_3Zn_8 is formed of a pseudo-hexagonal close-packed structure. The lithium–cadmium alloys have given rise to considerable controversy. It appears, however, that both sides may be right: that the quenched LiCd has a true cæsium chloride structure, as A. Baroni [43] maintains, and that the tempered alloy has the more ordered NaTl structure.[44]

Two more compounds, $LiHg_3$ and Li_3Hg, have been established, and hexagonal and cubic structures have been determined.[45] LiAl [46] has an NaTl structure. The structure Mg_3Al_2 is of exceptional interest, for here among the A-group metals we have the same complicated structure with 58 atoms as is found in α-manganese and β-chromium. F. Laves, K. Löhberg, and P. Bahlfs [47] have made a complete determination of the structure; each magnesium atom is surrounded by 4—7 other magnesium atoms at a distance of 2·95—3·35 Å., and by 6—12 aluminium atoms at a distance of 2·9—3·2 Å. The aluminium atom, on the other hand, besides its 8 magnesium neighbours, has 2 aluminium neighbours, one at 2·82 and one at 2·65 Å. This distance is very much shorter than the Al–Al distance of 2·86 in the metal, and indicates the extent of a special binding force of the aluminium, such as occurs in metallic gallium. In the system aluminium–zinc, it appears that at high temperatures zinc may dissolve in aluminium to the extent of 48% at 350°, but at lower temperatures this solid solution splits up into a β, aluminium-rich, and a γ, zinc-rich, portion.[48] The structure of Al_4Ba [49] is of some interest. It appears to be a tetragonal layer lattice in which each barium atom is surrounded by 16 aluminium atoms, and each of the latter is surrounded by 4 barium and 4 or 5 aluminium atoms.

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[41] G. Grube, H. V. Zeppelin, and H. Bumm, *Z. Elektrochem.*, 1934, **40**, 143, 160; *A.*, 1934, 591.

[42] E. Zintl and A. Schneider, *ibid.*, 1935, **41**, 764.

[43] *Ibid.*, 1934, **40**, 565; *Atti R. Accad. Lincei*, 1934, [vi], **19**, 507; *A.*, 1934, 954.

[44] E. Zintl and A. Schneider, *Z. Elektrochem.*, 1934, **40**, 107.

[45] *Idem, ibid.*, 1935, **41**, 771.

[46] G. Komovsky and A. Maximov, *Z. Krist.*, 1935, **92**, 275.

[47] *Nach. Ges. Wiss. Göttingen*, 1934, **1**, 67.

[48] E. Schmid and G. Wassermann, *Z. Metallk.*, 1934, **26**, 145; *A.*, 1934, 1064; E. A. Owen and J. Iball, *Phil. Mag.*, 1934, [vii], **17**, 433; *A.*, **1934**, **356**.

The structure of gallium proposed by Laves [50] has been confirmed by Bradley.[51] He finds the cell dimensions to be 4·5167, 4·5107, and 7·6448 Å., the smallest known departure from tetragonal symmetry.

A. Ölander [52] has studied thallium compounds extensively by electrochemical and *X*-ray methods. The Tl–Hg system contains two compounds of the approximate composition Hg_3Tl and $HgTl_8$ with face-centred and body-centred cubic lattices respectively. The Pb–Tl system shows an extended solid solution from lead up to 92% of thallium, with some evidence for ordered structure of Tl_7Pb. The compound Bi_2Tl has a very interesting structure. The cell is hexagonal, $a = 5{\cdot}67$, $c = 3{\cdot}37$ Å., and contains a graphite-like arrangement of bismuth-hexagons in the holes of which, above and below, fit the thallium atoms. The structure of $TlSb_2$, determined by F. R. Morral and A. Westgren,[53] has a somewhat deformed cæsium chloride super-lattice; each antimony atom has four thallium neighbours at 3·1 Å., one at 3·38, and four more at 3·48 Å. The Sn–As system [54] has been shown to have only one compound, SnAs, with the sodium chloride structure as with SnSb. This compound has, however, a range of solid solubility from 34 to 48% (by wt.) of arsenic. It is interesting to note that the lattice dimensions increase in both directions on departing from the ideal configuration.

The structure of the alloys of the rare-earth metals has been extended chiefly by the work of A. Rossi and his collaborators.[55] Two types only are found, the cubic face-centred type AB_3, where A = Pr, La, or Ce, and B = Mg, Sn, Tl, or Pb, and the cæsium chloride type found for NdAl and LaMg. Praseodymium is found to have two structures: α-Pr, face-centred cubic, $a = 5{\cdot}10$, and β-Pr, hexagonal close-packed, $a = 5{\cdot}17$, $c/a = 1{\cdot}633$.

Adamantine Compounds.—Carbides, nitrides, etc. Our knowledge of the structure of the non-metallic carbides and nitrides has been much advanced by the work of M. von Stackelberg. According to him,[56] these structures can be most readily understood by considering them as ionic, carbon, nitrogen, etc., functioning as large anions C^{4-}, N^{3-}, or in higher carbides as the C_2^{2-} or C_2^{4-} ions. These ions are in general close-packed, the metal ions occupying octahedral or tetrahedral holes. Thus, Be_2C [57] has an antifluorite structure, each beryllium having four carbon neighbours, and each carbon eight beryllium neighbours. This classification is borne out by the action of water,[58] carbides with separated atoms yielding methane, those with carbon pairs, acetylene, and Mg_2C_3, allylene, possibly owing to C_3 groups in the crystal.

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[49] K. R. Andress and E. Alberti, *Z. Metallk.*, 1935, **27**, 126.

[50] See *Ann. Reports*, 1933, **30**, 293.

[51] *Z. Krist.*, 1935, **91**, 303.

[52] *Z. physikal. Chem.*, 1935, [*A*], **171**, 425; 1934, **168**, 274; *A.*, 1934, 724; *Z. Krist.*, 1934, **89**, 89; *A.*, 1934, 1301.

[53] *Svensk Kem. Tidskr.*, 1934, **46**, 153; *A.*, 1934, 1296.

[54] W. H. Willott and E. J. Evans, *Phil. Mag.*, 1934, [vii], **18**, 114; *A.*, 1934, 953.

[55] *Gazzetta*, 1934, **64**, 748, 774, 832, 955; *A.*, 1935, 151, 152; A. Rossi and A. Iandelli, *Atti R. Accad. Lincei*, 1934, [vi], **19**, 415; *A.*, 1934, 720; C. W. Stillwell and E. E. Jukkola, *J. Amer. Chem. Soc.*, 1934, **56**, 56; *A.*, 1934, 243.

The structure of Li_3N [59] is not, as previously supposed,[60] similar to that of ammonia; it consists of a simple hexagonal arrangement of nitrogen atoms with lithium atoms lying, some between two and some between three nitrogen atoms.[61] Ca_3N_2 may have a similar structure. The structure of Al_4C_3 [62] has been most fully worked out: it has a rhombohedral cell, $a = 3{\cdot}325$, $c = 24{\cdot}94$ Å.; the structure is a layer one, three layers of carbon atoms being interleaved with four of aluminium. Each of the latter is surrounded by four carbon atoms at a distance of 1·9—2·0 Å. (sum of atomic radii, 2·03 Å.), while the carbon atoms have either five or six aluminium neighbours. The closely related Al_5C_3N [63] has a very similar hexagonal structure, a layer of AlN being sandwiched between the Al_4C_3 layers. More definitely adamantine is boron carbide, B_4C, examined by F. Laves.[64] L. Pauling and S. Weinbaum [65] have determined the parameters of the framework structure B_6Ca [66] and find that each boron atom is exactly 1·716 Å. from five others.

Graphite and its compounds have been much studied. It is the best layer lattice that we know, and the two-dimensional macromolecules of which it is made can enter into many combinations without affecting its structure. That all forms of carbon except diamond contain such molecules has been conclusively shown by

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[56] *Z. physikal. Chem.*, 1934, [*B*], **27**, 53.

[57] M. von Stackelberg and F. Quatram, *ibid.*, p. 50.

[58] J. Schmidt, *Z. Elektrochem.*, 1934, **40**, 170; *A.*, 1934, 614.

[59] E. Zintl and G. Brauer, *ibid.*, 1935, **41**, 102.

[60] R. Brill, *Z. Krist.*, 1927, **65**, 94.

[61] H. Hartmann and H. J. Fröhlich, *Z. anorg. Chem.*, 1934, **218**, 190; *A.*, 1934, 741.

[62] M. von Stackelberg and E. Schnorrenberg, *Z. physikal. Chem.*, 1934, [*B*], **7**, 37.

[63] M. von Stackelberg and K. F. Speiss, *ibid.*, 1935, [*A*], **175**, 140.

[64] *Nach. Ges. Wiss. Göttingen*, 1934, **1**, 57.

[65] *Z. Krist.*, 1934, **87**, 181; *A.*, 1934, 243.

[66] See *Ann. Reports*, 1933, **30**, 394.

B. E. Warren[67] by Patterson–Fourier methods (see p. 195). The finest and most amorphous carbon black is found to consist of crystallites about 60 Å. wide by 10 Å. thick, containing only two or three layers of 400 rings each. Other work on different types of graphite[68] confirms this, and also shows that as the particle size diminishes, the inter-layer distance increases from 3·4 to 3·6 Å. The magnetic anisotropy of graphite is even greater than has been supposed. Indian workers[69] have shown that the principal susceptibilities are — 22·8 and — 0·4 parallel to and perpendicular to the hexagonal axes. U. Hofmann[70] has given a general survey of the reactions of graphite; in particular, of the formation of graphite oxide by the addition of oxygen atoms (probably hydroxy-groups) on each side of the molecule. A series of graphite sulphates has also been prepared[71] with sulphate groups between every two, four, six, etc., graphite planes. Carbon subfluoride, CF, is also a graphite compound which has largely lost its metallic character.[72]

Iodides, phosphides, etc. The iodides and mercuri-iodides of silver and copper have proved to be of great theoretical interest (see p. 188). The β- and the γ-form of silver iodide, stable between 146—136° and below 135°, have zinc blende and wurtzite structures respectively, with densities $5{\cdot}71_3$ and $5{\cdot}69_5$.[73] They may be considered as close-packed iodine lattices with metal atoms in tetrahedral interstices. The α-form, investigated by L. W. Strock,[74] has a body-centred cell, $a = 5{\cdot}034$ Å., with a density of 6·00 and two molecules per cell. The silver atoms cannot be placed; they are, so to speak, in a gaseous state between the iodine atoms. This structure goes far to explain the large self-diffusion, electric conductivity, and plasticity of the crystals, but the structure is so anomalous that it calls for further physical and crystallographic investigation. A similar but less marked indeterminacy has been found in the cubic ($>90°$) modification of silver and cuprous mercuri-iodides studied by J. A. A. Ketelaar:[75, 76] neither mercury nor silver atoms are in fixed positions in the cubic close-packed iodine lattice.

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[67] *J. Chem. Physics*, 1934, **2**, 551; *A.*, 1934, 1160.

[68] P. C. Mukherjee, *Z. Physik*, 1934, **88**, 247; *A.*, 1934, 577; M. Miwa, *Sci. Rep. Tôhoku Imp. Univ.*, 1934, **23**, 242; *A.*, 1934, 835; W. S. Wesselowski and K. W. Wassiliew, *Z. Krist.*, 1934, **89**, 156.

[69] K. S. Krishnan, *Nature*, 1934, **133**, 174; B. C. Guha and B. P. Ray, *Indian J. Physics*, 1934, **8**, 345.

[70] *Kolloid-Z.*, 1934, **69**, 351; *A.*, 1935, 163; U. Hofmann, A. Frenzel, and E. Csalán, *Annalen*, 1934, **510**, 1; *A.*, 1934, 614; cf. H. Thiele, *Z. Elektrochem.*, 1934, **40**, 26; *A.*, 1934, 262.

[71] A. Frenzel and U. Hofmann, *ibid.*, p. 511; *A.*, 1934, 978.

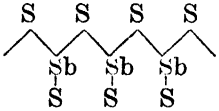
[72] O. Ruff and O. Bretschneider (with F. Ebert), *Z. anorg. Chem.*, 1934, **217**, 1; *A.*, 1934, 378.

[73] N. H. Kolkmeijer and J. W. A. van Hengel, *Z. Krist.*, 1934, **88**, 317; *A.*, 1934, 1161; L. Helmholz, *J. Chem. Physics*, 1935, **3**, 740.

[74] *Z. physikal. Chem.*, 1934, [*B*], **25**, 441; *A.*, 1934, 834.

The structures of a number of phosphides and arsenides have been determined by M. von Stackelberg and R. Paulus.[77] Zn_3P_2, Zn_3As_2, Cd_3P_2, and Cd_3As_2 have not, as was previously supposed, a cubic, but a tetragonal pseudo-cubic, structure in which the metal atoms fit in the tetrahedral holes of a slightly deformed cubic close packing. ZnP_2, CdP_2, and $ZnAs_2$ have more complicated tetragonal structures. The structures of Cu_2Sb and Fe_2As are identical; they may be considered as layers of cubic close-packed CuSb, Cu_2, CuSb held together by attractions between the copper in one layer and the antimony in the next.[78] The monophosphides and arsenides of Mn, Fe, Co[79] are shown to have a modified NiAs structure, while FeP_2 has a marcasite structure.[80]

Sulphides and sulpho-salts. The work of the past two years has helped to confirm and extend the general classification put forward in the Report for 1933 (p. 396). W. Hofmann[81] has studied, in particular, the sulphantimonates, and shown that where the ratio $Sb : S < 1 : 3$, there is a tendency to form fibrous crystals with a chain period 3·8—4·3 Å. corresponding to the chain molecule



There is a general tendency for antimony to have three close sulphur neighbours, copper four, and lead six.

A. Ferrari has shown that the series, sclericlase $PbAs_2S_4$ to dufresnoyite $Pb_2As_2S_5$, is isomorphous and shows a strong resemblance to orpiment As_2S_3 and to wolfsbergite $CuSbS_2$.[82] Many more sulphides are found to be related to the zinc blende 4-co-ordination type. Binnite $(Cu,Fe)_{12}As_4S_{13}$, analysed by L. Pauling and E. W. Neuman,[83] may be taken as the type of the tetrahedrite minerals; here again, the arsenic atoms are attached to 3 sulphur atoms only. Colusite $(Cu, Fe, Mo, Sn)_4(S, As, Te)_{3-4}$[84] has a statistical zinc blende

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[75] *Z. Krist.*, 1934, **87**, 436; *A.*, 1934, 947.

[76] *Z. physikal. Chem.*, 1934, [*B*], **26**, 327; 1935, **30**, 53.

[77] *Ibid.*, **28**, 427.

[78] E. Elander, G. Hägg, and A. Westgren, *Arkiv Kemi, Min. Geol.*, 1935, **12**, [*B*], 1.

[79] K. E. Fylking, *ibid.*, 1934, **11**, [*B*], 48.

[80] K. Meisel, *Z. anorg. Chem.*, 1934, **218**, 360; *A.*, 1934, 947.

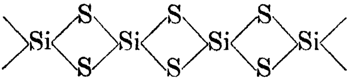
[81] *Z. Krist.*, 1935, **92**, 161.

[82] A. Ferrari and R. Curti, *Per. Min.*, 1934, **5**, 3.

[83] *Z. Krist.*, 1934, **88**, 54; *A.*, 1934, 1060.

[84] W. H. Zachariasen, *Amer. Min.*, 1933, **18**, 534; *A.*, 1934, 720.

structure. Stannite, Cu_2FeSnS_4,[85] belongs to the chalcopyrite type, while enargite, Cu_3AsS_4,[86] is more closely related to wurtzite but contains separate AsS_4 groups. Tetradymite, Bi_2Te_2S,[87] has a very interesting structure with successive layers of S–Bi–Te–Te–Bi–S all in 6-co-ordination. For other sulphides examined, only references can be given.[88] Silicon disulphide has a structure of a new type. W. Bussem, H. Fischer, and E. Gruner[89] have found that



it contains chains of tetrahedra sharing pairs of sulphur atoms and not a three-dimensional network as in SiO_2.

Ionic Compounds.—Halides. E. Zintl and A. Harder[90] have compared the structures of LiH^1 and LiH^2, the respective lattice dimensions being 4·085 and 4·065 ± 0·001 Å. This means that the radius of the hydrogen ion is changed from 1·27 to 1·26, or 0·8% effectively, by the lower zero-point energy of deuterium. They[91] have further examined the hydrides of calcium, strontium and barium, and shown that these possess a pseudohexagonal structure intermediate between a CaF_2 and a layer lattice. Each strontium ion has three hydrogen neighbours at 2·35 and four at 2·71 Å. (sum of ionic radii, 2·52 Å.).

E. B. Thomas and L. J. Wood[92] have examined the reactions between alkali halide pairs. In every case but two, the final product contains the pair with the smallest radius sum and therefore with the largest lattice energy, *e.g.*, $NaBr + KCl \longrightarrow NaCl + KBr$. In the two cases indeterminate, $KBr + RbI$ and $RbCl + CsBr$, homogeneous solid solutions are formed.

Although calcium chloride has a slightly deformed rutile structure,[93] the halides of the other bivalent elements cadmium, cobalt, and nickel have been shown[94] to have either the cadmium chloride or the cadmium iodide structure or to alternate between them (see p. 188). G. Bruni and A. Ferrari[95] have discussed the extended isomorphism of halide crystals based on close packed halogen ions.[96] Parallel intergrowths have been found between potassium and lead chlorides.[97]

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[85] L. O. Brockway, *Z. Krist.*, 1934, **89**, 434; *A.*, 1935, 152.

[86] L. Pauling and S. Weinbaum, *ibid.*, **88**, 48; *A.*, 1934, 1060.

[87] D. Harker, *ibid.*, **89**, 175.

[88] M. J. Buerger, *Amer. Min.*, 1935, **20**, 36; *A.*, 323; F. Weibke and J. Laar (with K. Meisel), *Z. anorg. Chem.*, 1935, **224**, 49; *A.*, 1322; G. R. Levi and A. Baroni, *Z. Krist.*, 1935, **92**, 210; B. Gossner and O. Kraus, *Centr. Min.*, 1934, [*A*], **1**, 1; B. Gossner, *ibid.*, 1935, [*A*], **11**, 321.

[89] *Naturwiss.*, 1935, **23**, 740.

[90] *Z. physikal. Chem.*, 1935, [*B*], **28**, 478.

[91] *Z. Elektrochem.*, 1935, **41**, 33.

[92] *J. Amer. Chem. Soc.*, 1935, **57**, 822; *A.*, 832; 1934, **56**, 92; *A.*, 1935, 265.

[93] A. K. Van Bever and W. Nieuwenkamp, *Z. Krist.*, 1935, **90**, 374.

[94] J. M. Bijvoet and W. Nieuwenkamp, *ibid.*, 1933, **86**, 466; *A.*, 1934, 16; J. A. A. Ketelaar, *ibid.*, 1934, **88**, 26; *A.*, 1934, 1060; H. Grime and J. A. Santos, *ibid.*, p. 136; *A.*, 1934, 1161.

H. Braekken and W. Scholten [98] have determined the structure of mercuric chloride. It is a fairly definite molecular lattice with a trace of layer formation, but along (120) and not along (001), as in mercuric bromide. The mercury halides are a good example of the transition from a purely ionic type, HgF_2, to a molecular type $HgCl_2$, and through a molecular layer lattice, $HgBr_2$, to a true layer lattice HgI_2,[99] with increasing polarisability of the anion.

F. A. Bannister and M. H. Hey [1] have shown that the structure of matlockite, PbFCl,[2] and of PbFBr is a type structure for oxyhalides—such as BiOCl(Br,I), and probably others such as FeOCl.

Simple oxides. E. Zintl, A. Harder, and B. Dauth [3] have examined the compounds $(Li,Na,K)_2(O,S,Se,Te)$. All crystallise with the fluorite structure, but there are considerable variations from accepted ionic radii. (Mlle.) B. Ruhemann [4] has shown that the thermal anomaly of manganese oxide at – 115° to – 119° is accompanied by a change of lattice constant from 4·426 to 4·416. Similar anomalies have been reported for FeO and Fe_3O_4, where they are accompanied by magnetic changes. These changes, though similar to those produced by rotation of molecules, are here probably due to electronic changes in the unfilled electron levels of iron and manganese. Palladous oxide has been shown to have 4-square co-ordination like its sulphide.[5] The structure of cupric oxide, tenorite,[6] is a distorted monoclinic variety of the same structure : each copper atom is surrounded by 4 oxygen atoms in a rectangle, Cu–O = 1·95. Another form is reported.[7]

Considerable dispute between electron and *X*-ray methods has arisen over the lattice dimension of zinc oxide. G. I. Finch

[95] *Z. Krist.*, 1934, **89**, 499.

[96] See *Ann. Reports*, 1931, **28**, 285.

[97] M. Mehmel and W. Nespital, *Z. Krist.*, 1934, **88**, 345; *A.*, 1934, 1161.

[98] *Ibid.*, **89**, 448.

[99] W. S. Gorski, *Physikal. Z. Sovietunion*, 1934, **5**, 367; P. Jolibois and G. Fouretier, *Compt. rend.*, 1933, **197**, 1322; *A.*, 1934, 41.

[1] *Min. Mag.*, 1934, **23**, 587; 1935, **24**, 49; *A.*, 1934, 1197.

[2] See *Ann. Reports*, 1933, **30**,, 399.

[3] *Z. Elektrochem.*, 1934, **40**, 588.

[4] *Physikal. Z. Sovietunion*, 1935, **7**, 590; *A.*, 1307.

[5] See *Ann. Reports*, 1933, **30**, 396.

[6] G. Tunell, E. Posnjak, and C. J. Ksanda, *Z. Krist.*, 1935, **90**, 120.

[7] C. A. Murison, *Phil. Mag.*, 1934, [vii], **17**, 96; *A.*, 1934, 134.

and H. Wilman [8] find by electrons, $a = 3{\cdot}258$, $c = 5{\cdot}239$, $\pm\ 0{\cdot}005$ Å., whereas C. W. Bunn finds by X-rays $a = 3{\cdot}2426 \pm 0{\cdot}0001$, $c = 5{\cdot}1948 \pm 0{\cdot}0003$ Å.[9] This apparent discrepancy may be due to the dispersion of the electron waves, but another cause has recently been shown by V. E. Cosslett [10] to be that the dimensions of zinc oxide prepared as smoke vary with time, a changing from 3·234 to 3·279, and c from 5·221 to 5·367 in 18 months owing to slow relief of quenching strain.

Complex oxides. G. Hägg [11] has studied the properties of the cubic tungsten bronzes $Na_{1-0{\cdot}3}WO_3$.[12] They may be considered as interstitial solutions of Na in WO_3 or as solid solutions of $Na^+W^{5+}O_3$ in $W^{6+}O_3$. All have a sub-metallic character (surface colour, conductivity decreasing with temperature) which becomes more marked as the percentage of sodium falls; when Na : W < 0·3 : 1, the amount of Na is not sufficient to stabilise the open cubic structure and it becomes tetragonal, exactly as in the corresponding case of the silicates ultramarine [13] and sodalite.[14] Corresponding suboxides of tungsten, W_8O_{23} and W_4O_{11}, have been examined;[15] they may be, however, hydrogen bronzes $H_{0{\cdot}5}WO_3$ and $H_{0{\cdot}25}WO_3$.

The Mn_xO_y system also shows continuous variations of structures on taking up and losing oxygen.[16] Mn_2O_3 exists in two forms, β-Mn_2O_3, bixbyite C type, and α-Mn_2O_3, probably related to Mn_3O_4 as γ-Fe_2O_3 is to Fe_3O_4. Nd_2O_3 and La_2O_3 [17] have now been prepared of the C (cubic) type.

E. J. W. Verwey [18] has specially studied the γ-Fe_2O_3 and γ-Al_2O_3 structures. The relation of these to the spinels has been studied by E. J. W. Verwey,[18] G. Hägg,[19] E. Kordes,[20] and others.[21] It has been shown, from considerations both of atomic dimensions and of intensities, that the previously assumed oxygen addition [22] to the cell is incorrect, and that, instead, there are $21\frac{1}{3}$ cations distributed statistically over the 24 (8 tetrahedral and 16 octahedral) vacant positions in the cell. Small quantities of lithium stabilise this structure as $LiAl_5O_8$ [20] in the limit. The γ'-Al_2O_3 formed by surface oxidation is an even more statistical structure with the same oxygen arrangement; the $21\frac{1}{3}$ aluminium atoms occupy 32 positions, or in the reduced cell which results, $2\frac{2}{3}$ atoms occupy the 4 positions of the rock salt lattice. A similar structure, but with $Li^{+}_{2\frac{2}{3}}$ and $Ti^{4+}_{1\frac{1}{3}}$ ions instead of $Al^{3+}_{2\frac{2}{3}}$ is that of Li_2TiO_3,[20] which is fully miscible with MgO and $LiFeO_2$ (see p. 188).

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[8] *J.*, 1934, 751; *A.*, 1934, 835.

[9] *Proc. Physical Soc.*, 1935, **47**, 835; *A.*, 1307.

[10] *Nature*, 1935, **136**, 988.

[11] *Z. physikal. Chem.*, 1935, [*B*], **29**, 192; *Nature*, 1935, **135**, 874.

[12] See *Ann. Reports*, 1933, **30**, 400.

[13] F. M. Jaeger, *Bull. Soc. franç. Min.*, 1930, **53**, 183.

[14] T. F. Barth, *Z. Krist.*, 1932, **83**, 605.

[15] F. Ebert and H. Flasch, *Z. anorg. Chem.*, 1934, **217**, 95; *A.*, 1934, 378.

[16] P. Dubois, *Compt. rend.*, 1934, **199**, 1416; *A.*, 1935, 181; M. Le Blanc and G. Wehner, *Z. physikal. Chem.*, 1934, [*A*], **168**, 59; *A.*, 1934, 378.

[17] K. Löhberg, *ibid.*, 1935, [*B*], **28**, 402.

[18] *J. Chem. Physics*, 1935, **3**, 592; *A.*, 1307; *Z. Krist.*, 1935, **91**, 65, 317; E. J. W. Verwey and M. G. van Brugger, *ibid.*, **92**, 136.

[19] *Z. physikal. Chem.*, 1935, [*B*], **29**, 95; G. Hägg and G. Söderholm, *ibid.*, p. 88.

[20] *Ibid.*, **91**, 193; **92**, 139.

[21] G. L. Clark, E. E. Howe, and A. E. Badger, *J. Amer. Ceram. Soc.*, 1934, **17**, 7; *A.*, 1934, 249.

E. Posnjak and T. F. W. Barth [23] have studied the hardly less extended haematite(Fe_2O_3)–ilmenite($FeTiO_3$) series. These are shown to be strictly isomorphous, as are the titanates of Mg, Mn, Co, Ni, and Cd (low-temperature form). The high-temperature form of $CdTiO_3$ belongs to the perovskite type, which has also very many members.[24]

Hydroxides. The past two years have shown great advances in our knowledge of the hydroxides.[25] As the numbers of structures analysed increased, the function of the hydrogen in binding together the hydroxy-groups attached to different cations was more fully recognised. J. D. Bernal and (Miss) H. D. Megaw [26] have summarised our knowledge on this point in a paper where all known hydroxide structures are discussed. It is found that the hydroxyl group varies in a continuous way from a quasi-isotropic group in alkali hydroxides to a definitely tetrahedral, water-like, group in the neutral and slightly acid hydroxides. The increasing polarising power of the cation drives the proton further from its own oxygen nucleus, and consequently increases its attraction for the negative regions in other hydroxyl groups. In this way, a bond, which may be called the hydroxyl bond, is formed, only less in strength than the hydrogen bond in acids (as shown by the O–O distance of 2·76 instead of 2·55 Å. as in acids). By the use of this conception, it has been possible to locate the positions of hydrogen atoms in a number of hydroxide structures, particularly in hydrargillite [27] where the six hydroxyls of different $Al(OH)_6$ groups form an irregular trigonal prism, six of whose sides, of length 2·75, 2·80, 2·82, and 2·94, 2·98, 3·10 Å., represent hydroxyl bonds, while the remaining three, of length 3·32, 3·38, and 3·46 Å., do not. Linking up of hydroxyl bonds explains the properties of the gels formed by neutral hydroxides, discussed from the structural point of view by R. Fricke.[28] The structure of boric acid has been completely determined by W. H. Zachariasen.[29] It consists of flat layers of BO_3 groups attached to each other by hydrogen or hydroxyl bonds, the O–O distance, 2·71, being nearer the requirements of the latter. The layers adhere by residual forces at a distance of 3·18 Å., agreeing with the cleavage and softness of the crystals. The hydrated boron phosphate, $B(OH)_3,(HO)_3PO$ may have a very similar structure.[30]

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[22] See *Ann. Reports*, 1933, **30**, 403.

[23] *Z. Krist.*, 1934, **88**, 265, 271; *A.*, 1934, 1162.

[24] A. Hoffmann, *Z. physikal. Chem.*, 1935, [*B*], **28**, 65; H. Rheinboldt, *J. pr. Chem.*, 1934, [ii], **139**, 318; *A.*, 1934, 587.

[25] Cf. *Ann. Reports*, 1933, **30**, 401.

[26] *Proc. Roy. Soc.*, 1935, [*A*], **151**, 384; *A.*, 1307.

[27] (Miss) H. D. Megaw, *Z. Krist.*, 1934, **87**, 185; *A.*, 1934, 352.

Telluric acid is also a hydroxy-acid, $Te(OH)_6$; its structure has been studied by B. Gossner and O. Kraus [31] and by L. Pauling.[32] In its two cubic and monoclinic (pseudocubic) forms it represents $Te(OH)_6$ octahedra bound together in different ways by hydroxyl bonds of length 2·76 Å. Recent work on zinc hydroxide [33] shows that the different reported crystalline forms have all the same structure.[34]

The oxy-hydroxide, BO(OH), has a definite crystalline form [35] but its structure has not been determined. The structures of α- and γ-Al(Fe)O(OH), diaspore (goethite) and böhmite (lepidocrocite), have been determined by S. Goldsztaub [36] and F. J. Ewing.[37] Both contain hydroxyl bonds, but whereas the α-forms are fairly compact, the γ-forms are true layer lattices of the type of the oxychlorides (see p. 210). The calcium aluminates form complex hydrates and hydroxy-compounds.[38] The structure of one of these, hydrocalumite,[39] $Ca_2Al(OH)_7,3H_2O$, has been partially analysed; it consists of alternate layers of $Al(OH)_72H_2O$ and Ca_2H_2O.

Borates and silicates. The chief interest with silicate investigations in the past two years has been concerned with those silicates with extended three- and two-dimensional structures, *i.e.*, with silica in its various forms, with zeolites, and the clay minerals. Now that the main outline of silicate structure is known, its utility is being appreciated in the technical sphere; particularly in America, much work is being done on *X*-ray structures in connexion with the glass and ceramic industries, which involves not only the study of those silicates but of the analogous boron compounds which also form extended frame-work structures. N. W. Taylor and S. S. Cole[40] have succeeded in producing crystalline B_2O_3, hitherto known only as a glass, by careful dehydration of H_3BO_3. It appears to be cubic, $a = 10{\cdot}04$, with 16 molecules per cell, but its exact structure is not known. It melts at 294° ± 1° to a very viscous liquid which hardens to glass at 276°. On melting, there is an increase in density from 1·805 to 1·844, showing that, like ice, but unlike silica, the arrangement of the solid has a lower effective co-ordination than that of the liquid.

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[28] *Kolloid-Z.*, 1934, **69**, 312; *A.*, 1935, 162.

[29] *Z. Krist.*, 1934, **88**, 150; *A.*, 1934, 1161.

[30] E. Gruner, *Z. anorg. Chem.*, 1934, **219**, 181; *A.*, 1934, 1081.

[31] *Z. Krist.*, 1934, **88**, 298; *A.*, 1934, 1161.

[32] *Ibid.*, 1935, **91**, 367.

[33] K. Petrescov, *ibid.*, p. 505; (Miss) H. D. Megaw, *ibid.*, 1935, **90**, 283.

[34] See *Ann. Reports*, 1933, **30**, 401.

[35] H. Menzel, H. Schulz, and H. Deckert, *Z. anorg. Chem.*, 1934, **220**, 49.

[36] *Bull. Soc. franç. Min.*, 1935, **58**, 6.

[37] *J. Chem. Physics*, 1935, **3**, 203; cf. M. Deflandre, *Bull. Soc. franç. Min.*, 1932, **55**, 140; K. Takane, *Proc. Imp. Akad. Tokyo*, 1933, **9**, 113; F. J. Ewing, *J. Chem. Physics*, 1934, **3**, 420.

[38] R. Salmoni, *Gazzetta*, 1935, **64**, 719.

[39] C. E. Tilley [with (Miss) H. D. Megaw and M. H. Hey], *Min. Mag.*, 1934, **23**, 607; *A.*, 1934, 1197.

A study of the borates[41] shows that, like the silicates, the extended networks and chains may be found; but no complete structures have been worked out. M. Mehmel[42] has made an elaborate study of boracite, $Mg_6Cl_2B_{14}O_{26}$, which above 265° is cubic, $a = 12{\cdot}1$ Å., and below, rhombic, pseudo-cubic; but the exact structure has not been determined—it is apparently also of a framework character. The structure of jeremejewite, $BAlO_3$,[43] has been studied but proves to be unexpectedly complex. The structures of the phosphates and arsenates of boron, aluminium, and iron, as Goldschmidt predicted, are similar to those of silica. BPO_4 and $BAsO_4$[44] have a cristobalite structure with both atoms tetrahedrally surrounded by oxygen. M. Strada[45] maintains that $AlPO_4$ and $AlAsO_4$ have the same structure. H. F. Huttenlocher[46] and F. Machatschki[47] have, however, shown that normally they are of the quartz type with a doubled *c* axis on account of the difference of the two atoms replacing silicon. V. Caglioti[48] has shown that $FePO_4$ has the same structure, but the $AlPO_4$ may be dimorphous with the high-temperature cristobalite type, thus reconciling all the other workers' results. T. F. W. Barth[49] has gone further, and shown the aluminites and ferrites, $K_2Al_2O_4$ and $(K_2, Rb_2, Pb)(Fe_2O_4)$, also to be of the cristobalite type with the large atoms in the interstices as in carnegeite.[50]

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[40] *J. Amer. Chem. Soc.*, 1934, **56**, 1648; *A.*, 1934, 947; *J. Amer. Ceram. Soc.*, 1935, **18**, 55.

[41] S. S. Cole, N. W. Taylor, and S. R. Scholes, *ibid.*, p. 79; S. S. Cole, S. R. Scholes, and C. R. Amberg, *ibid.*, p. 58.

[42] *Z. Krist.*, 1934, **87**, 239; **88**, 1; *A.*, 1934, 387, 1060.

[43] B. Gossner and O. Kraus, *Centr. Min.*, 1934, [*A*], **11**, 348.

[44] G. E. R. Schulze, *Z. physikal. Chem.*, 1934, [*B*], **24**, 215; *A.*, 1934, 352.

[45] *Gazzetta*, 1934, **64**, 653; *A.*, 1934, 1296.

[46] *Z. Krist.*, 1935, **90**, 508; *A.*, 1194.

[47] *Ibid.*, p. 314; *A.*, 1060.

[48] *Atti R. Accad. Lincei*, 1935, **22**, 146.

[49] *J. Chem. Physics*, 1935, **3**, 323.

M. J. Buerger has discussed the stability fields for the different forms of SiO_2.[51] The three forms, quartz, tridymite, and cristobalite, have increasingly empty spaces in the structure; consequently, the addition of foreign atoms with appropriate silicon substitutions has the effect of stabilising the higher-temperature forms. The general formula for such silicates can be written

$$Q^{q}_{(4-m)n/9}\left|\begin{array}{c}Si_{2-n}\\ M^{m}_{n}\end{array}\right|O_4$$

Where M represents the atom substituting the silicon, usually Al^3, and Q^q is the interstitial atom, usually Na^{1+} or Ca^{2+}. When $n = 1$, the tridymite structure, and when $n = 2$ the cristobalite structure, is stable at room temperatures.

A detailed analysis of low cristobalite structures has been made by W. Nieuwenkamp;[52] the Si–O–Si angle is found to be 150°. P'ei-Hsiu Wei,[54] in a redetermination of the α-quartz structure, found it to be 144°. Very interesting two-dimensional crystals of cristobalite, consisting essentially of polysynthetic twins, have been described as pseudomorphs of tridymite,[53] the (111) plane of the cristobalite corresponding in different positions to the (0001) plane of the latter. Further work has been done on the formation of cristobalite and the coagulation of silica gels.[55]

B. E. Warren has made a very thorough study of the structure of silica and other glasses by means of X-rays.[56] The new methods of crystal analysis (see p. 195) make it possible to determine the relative statistical position of the silicon, oxygen, and other atoms. The glasses of SiO_2, GeO_2, BeF_2 give essentially the same pattern. The silicon atom has six tetrahedral oxygens at 1·60, four more silicon neighbours at 3·20, and twelve more SiO_2 groups at 5·20 Å. In the case of the soda glasses, a certain number of oxygen atoms are attached to only one silicon atom, but to several sodium atoms, each of which has on the average two oxygen neighbours at 2·35 and two silicons at 3·45 Å.

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[50] See *Ann. Reports*, 1933, **30**, 406.

[51] *Z. Krist.*, 1935, **90**, 186.

[52] *Ibid.*, **92**, 82.

[53] *Ibid.*, **90**, 377.

[54] *Ibid.*, **92**, 355.

[55] F. P. Dwyer and D. P. Mellor, *J. Proc. Roy. Soc. N.S.W.*, 1934, **68**, 47; *A.*, 1935, 324; **67**, 420; *A.*, 1934, 947; M. O. Charmandarian and V. K. Markov, *Ukrain. Chem. J.*, 1933, **8**, 1; *A.*, 1244.

[56] *Physical Rev.*, 1934, [ii], **45**, 657; *A.*, 1934, 834; B. E. Warren and C. F. Hill, *Z. Krist.*, 1934, **89**, 481; B. E. Warren and A. D. Loring, *J. Amer. Ceram. Soc.*, 1935, **18**, 269; *A.*, 1308; cf. H. Hollenweger and H. Rumpett, *Angew. Chem.*, 1933, **46**, 662; *A.*, 1933, 1247.

Electron diffraction has also been applied to the study of glasses.[57] N. A. Schischakov has obtained the rather surprising result that very finely powdered silica glass shows sharp lines, indicating either the presence of small crystals of cristobalite in normal glass, or more probably, the rapid devitrification of glass when ground to a fine powder.

Structural work on the felspars has been continued.[58] The sanidine type [59] is found to hold for the K–Ba felspars. The albite–anorthite series ($NaAlSi_3O_8 \longrightarrow CaAl_2Si_2O_8$) show a doubling of the unit cell when the number of calcium atoms is greater than that of sodium.

The structure of the zeolites has been particularly well studied with special relation to their base-exchange properties; a general picture of them is given in an important paper by W. H. Taylor.[60] The mode of binding the unattached cations and the water molecules is discussed, and it is found possible to place the water molecules in such a way as to specify the tetrahedral positive and negative linkings postulated by Bernal and Fowler.[61] J. Wyart [62] has determined the structure of chabazite and other zeolites, and an important series of papers has been produced by F. A. Bannister and M. H. Hey [63] correlating the chemical and structural properties of the zeolites. The deformed Al–Si framework of the structures of hauyn and nosean, $Na[Al_6Si_6O_{24}]SO_4$, has been studied by Machatschki.[64]

Clay Minerals.—The structure of the clay minerals has excited much interest, both scientific and technical, in connexion with ceramics and soils. A general account of the *X*-ray work is given by U. Hofmann,[64a] and a more popular historical survey by C. E. Marshall. [65] Owing to the fine-grained nature of clays, the problem offers great difficulties, but *X*-ray methods have succeeded at least in ordering an apparently bewildering mass of data.

J. W. Gruner [66] R. C. MacMurchy,[67] M. Mehmel,[68] and others[69] have made more or less complete structure analyses. There are roughly three series of clay minerals containing treble, double, and single $(SiAl)_2O_5$ and $Al_2Mg_3(OH)_6$ hexagonal layers. They differ from the micas in that the layers are electrically neutral and are joined only by hydroxyl bonds. The treble series is represented by talc and pyrophyllite, with two Si_2O_5 layers on either side of $Mg_3(OH)_2$ layer (talc) or $Al_2(OH)_6$ layer (pyrophyllite). The formula may be written (indicating layers in turn by brackets) $(O_3)Si(O_2OH)\left\{\begin{matrix}Al_2\\Mg_3\end{matrix}\right.(O_2OH)Si(O_3)$. By intercalating an indefinite amount of water between such layers, the bentonite-thixotropic minerals are formed, montmorillonite (Mg), beidellite (Al), and nontronite (Fe^{3+}). The double series has a Si_2O_5 layer on one side only of the $Al_2(OH)_6$ layer. It is represented by kaolinite, $(O_3)Si(O_2OH)Al_2(OH)_3$, and also by nacrite, dickite, and meta-halloysite, which differ only in relative positions of the layers.

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[57] N. A. Schischakov, *Nature*, 1935, **136**, 514; *A.*, 1309; K. R. Dixit, *Physikal. Z.*, 1934, **35**, 141; *A.*, 1934, 352.

[58] W. H. Taylor, J. A. Darbyshire, and H. Strunz, *Z. Krist.*, 1934, **87**, 464; *A.*, 1934, 947.

[59] See *Ann Reports*, 1933, **30**, 405.

[60] *Proc. Roy. Soc.*, 1934, [*A*], **145**, 80; *A.*, 1934, 947.

[61] See *Ann. Reports*, 1934, **31**, 42.

[62] *Bull. Soc. franç. Min.*, 1933, **56**, 81; *A.*, 1934, 1197.

[63] *Min. Mag.*, 1933, **23**, 421; 1934, **23**, 483, 556; *A.*, 1934, 167, 508, 882; 1935, **24**, 99; *A.*, 1345.

[64] *Centr. Min.*, 1934, [*A*], **5**, 136.

[64a] See ref. (70), p. 207.

[65] *Science Progress*, 1936, [v], **30**, 422.

[66] *Z. Krist.*, 1934, **88**, 412; *A.*, 1934, 1162; *Amer. Min.*, 1934, **19**, 557; *A.*, 1934, 841; 1935, **20**, 475; *A.*, 1345.

[67] *Z. Krist.*, 1934, **88**, 420; *A.*, 1934, 1162.

[68] *Ibid.*, 1935, **90**, 53.

The single-layer clays are represented by halloysite, which has alternate silica alumina sheets joined by hydroxyl bonds,

$$\ldots (O_3)SiOH \ldots (OH)_3Al_2(OH)_3 \ldots ;$$

here also water can enter between the layers.

Optical and chemical research is keeping pace with the *X*-ray studies.[70] The formulæ of the minerals have been recalculated,[71] and the main types, kaolinite, dickite, and montmorillonite, synthesised by R. H. Ewell and H. Insley[72] by heating co-precipitated hydrogels under high pressure.

Complex Ions.—Diatomic and linear ions. The cyanide ion in AgCN does not rotate as it does in KCN,[73] but as C. D. West[74] has shown, it forms a unique linear lattice Ag–CN–Ag–CN in which there is considerable freedom of motion along the lines. The Ag–Ag distance is only 5·26 Å., so it is possible for Ag to be co-ordinately linked to the CN group at either end. The peroxide ion, O_2'', has been studied in the tetragonal SrO_2 and BaO_2, isomorphous with CaC_2.[75] The O–O distance is 1·31 (Pauling theoretical, 1·32; in persulphate, 1·46). The CNS group[76] is found to be bent at an

[69] B. Gossner, *Centr. Min.*, 1935, [*A*], **7**, 195; G. Nagelschmidt, *Z. Krist.*, 1934, **87**, 120; *A.*, 1934, 274.

[70] C. S. Ross and P. F. Kerr, *U.S. Geol. Survey*, 1934, Prof. Paper 185–G, 135; *A.*, 1935, 322; C. E. Marshall, *Z. Krist.*, 1935, **90**, 8.

[71] J. Holzner, *Chem. Erde*, 1935, **9**, 464; *A.*, 1220; C. E. Marshall, *Z. Krist.*, 1935, **91**, 433.

[72] *J. Res. Nat. Bur. Stand.*, 1935, **15**, 173; *A.*, 1333.

[73] See *Ann. Reports*, 1931, **28**, 295.

[74] *Z. Krist.*, 1934, **88**, 173; 1935, **90**, 555; *A.*, 1194.

[75] J. D. Bernal, E. Djatlowa, I. Kazarnowsky, S. Reichstun, and A. G. Ward, *ibid.*, 1935, **92**, 344.

[76] W. Büssem, P. Günther, and R. Tubin, *Z. physikal. Chem.*, 1934, [*B*], **24**, 1; *A.*, **1934**, 243.

angle of 130°, but the results are not conclusive. The I_3' group of NH_4I_3 has been carefully studied by R. C. L. Mooney;[77] it is practically straight but unsymmetrical, I–I distances being 3·10 and 2·82, a small but probably real difference. The I–I distance in different molecules is 4·1—4·28 and NH_4–I 3·7 Å. W. H. Zachariasen and Mooney[78] have determined the structure of the hypophosphite group H_2PO_2; it is a distorted tetrahedron with oxygen at two corners and hydrogen at the others; the O–P–O angle is 120°.

AX_3 *ions.* The structure of sodium hydrogen carbonate has also been determined by Zachariasen.[79] The CO_3 groups are linked in endless chains by a hydrogen bond of length 2·55 Å. Cæsium nitrate[80] has a pseudo-cubic structure resembling CsI and KIO_3. When NO_3' ions are not parallel or are rotating, they behave as if they were simple ions about equivalent to I′, as also do the ClO_4', MnO_4' ions.

AX_4 *ions.* The BF_4'[81] and BeF_4''[82] ions have been proved isomorphous with the ClO_4' and SO_4'' ions. $Ce_2(WO_4)_3$[83] has a scheelite, $CaWO_4$, structure with cerium atoms statistically distributed. $Na_6(SO_4)_2ClF$, sulphohalite, is shown by A. Pabst[84] to have an extremely compact cubic structure with SO_4 groups in the cube centre, Cl and F alternately at the corners, and Na atoms mid-way along the edges.

AX_6 *ions.* The structures of a large number of hexafluoro- and hexachloro-salts have been determined,[85] but in every case they confirm the octahedral character of the group. The ions OsO_2Cl_4''[86] and $OsNCl_5''$[87] also appear to be octahedral, the first in *trans*-configuration.

L. Pauling, H. P. Klug, and A. N. Winchell[88] have shown that swedenborgite, $NaBe_4SbO_7$, does not contain an SbO_7 group but consists of SbO_6 groups and Be_4O groups as in basic beryllium acetate.[89] $NaSb(OH)_6$,[90] though tetragonal, $a = 8{\cdot}00$, $c = 7{\cdot}86$, has essentially a sodium chloride structure of $Na^{\cdot}$ and $Sb(OH)_6'$ ions bound together in a face-centred cubic array by hydroxyl bonds as in $Te(OH)_6$, $a = 7{\cdot}83$ (see p. 213).

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[77] *Z. Krist.*, 1935, **90**, 143.

[78] *J. Chem. Physics*, 1934, **2**, 34; *A.*, 1934, 243.

[79] *Ibid.*, 1933, **1**, 634; *A.*, 1934, 16.

[80] L. Waldbauer and D. C. McCann, *ibid.*, 1934, **2**, 615; *A.*, 1934, 1161.

[81] J. L. Hoard and V. Blair, *J. Amer. Chem. Soc.*, 1935, **57**, 1985.

[82] P. L. Mukherjee, *Current Sci.*, 1934, **3**, 66; *A.*, 1934, 1162; R. Hultgren, *Z. Krist.*, 1934, **88**, 233; *A.*, 1934, 1162; J. L. Hoard and V. Blair, *J. Amer. Chem. Soc.*, 1935, **57**, 1985.

[83] J. Beintema, *Proc. K. Akad. Wetensch. Amsterdam*, 1935, **38**, 1011.

[84] *Z. Krist.*, 1934, **89**, 514.

[85] B. Gossner and O. Kraus, *ibid.*, **88**, 223; *A.*, 1934, 1161; J. A. A. Ketelaar, *ibid.*, 1935, **92**, 155; R. B. Corey, *ibid.*, 1934, **89**, 10; R. B. Corey and R. W. G. Wyckoff, *ibid.*, p. 469; G. Engel, *ibid.*, 1935, **90**, 341; J. L. Hoard and L. Goldstein, *J. Chem. Physics*, 1935, **3**, 645.

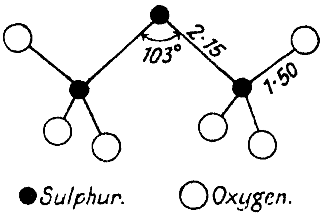
[86] J. L. Hoard and J. D. Grenko, *Z. Krist.*, 1934, **87**, 100; *A.*, 1934, 243.

[87] J. Verhulst, *Bull. Soc. chim. Belg.*, 1933, **42**, 359; *A.*, 1933, 1235.

[88] *Amer. Min.*, 1935, **20**, 492; *A.*, 1308.

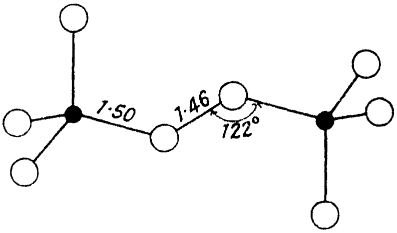
Pyro-, per-, and poly-ions. G. R. Levi and G. Peyronel [91] have studied the cubic salts (Si, Ti, Zr, Sn, Hf)P_2O_7 and have established the fact that the $P_2O_7^{4-}$ ion consists of two tetrahedra with a common corner and possessing the symmetry $\bar{3}$, trigonal axis. The strong effects of the quadrivalent ions may be in part responsible for this regularity. It would be interesting to see what the structure of the P_2O_7 ion would be in an alkali pyrophosphate. The trithionate ion $(S_3O_6)^{2-}$ is essentially, according to W. H. Zachariasen,[92] a pyro-ion in which the linking is done through a sulphur atom (see Fig. 3). The ion has one plane of symmetry through the three sulphur atoms, and a pseudo-plane perpendicular to it. The S–S distance is 2·15 Å. and the S–S–S angle 103°.

FIG. 3.



Structure of trithionate radical.

FIG. 4.



Structure of persulphate group.

The per-ions differ from the pyro-ions in that their oxygen atoms are joined, not shared. Zachariasen and his co-workers [93] have made a careful study with Fourier analyses of the persulphate ion in the ammonium, potassium, and cæsium salts. The two SO_4 groups are joined somewhat askew (Fig. 4). The link between them is somewhat longer than the theoretical value 1·31, but the accuracy claimed is ± 0·15 Å.

The ions Tl_2Cl_9''' [94] and W_2Cl_9''' [95] appear to be isomorphous, with a pair of metal atoms surrounded by octahedra of chlorine atoms which share one face. $Cs_3As_2Cl_9$ [96] does not, however, contain the ion As_2Cl_9, but should be written $(CsCl)_3(AsCl_3)_2$.

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[89] L. Pauling and J. Sherman, *Proc. Nat. Acad. Sci.*, 1934, **20**, 336.

[90] J. Beintema, *Proc. K. Akad. Wetensch. Amsterdam*, 1935, **38**, 1015.

[91] *Z. Krist.*, 1935, **92**, 190.

[92] *J. Chem. Physics*, 1934, **2**, 109; *A.*, 1934, 479; *Z. Krist.*, 1934, **89**, 529.

[93] R. C. L. Mooney and W. H. Zachariasen, *Physical Rev.*, 1933, [ii], **44**, 327; *A.*, 1935, 152; *Z. Krist.*, 1934, **88**, 63; *A.*, 1934, 1060; R. C. Keen, *ibid.*, 1935, **91**, 129.

[94] J. L. Hoard and L. Goldstein, *J. Chem. Physics*, 1935, **3**, 199; H. M. Powell and A. F. Wells, *J.*, 1935, 1008.

[95] C. Brosset, *Nature*, 1935, **135**, 874; *Arkiv Kemi, Min. Geol.*, 1935, **12**, [*A*], 1.

The heteropoly-acids and their salts have been further investigated, particularly by J. F. Keggin,[97] by *X*-ray powder methods.[98] In combination, they behave as very large spherical ions, in the interstices between which are found other ions and water molecules. It is interesting that the basicity of the different heteropoly-ions is fixed by the number of positive ions that can fit in the invariable calcium fluoride structure.

Organo-metallic and Co-ordinate Ions.—The dimethylthallium halides are an isomorphous series of a layer lattice type. H. M. Powell and (Miss) D. Crowfoot [99] have shown that the $H_3C–Tl–CH_3$ group is linear, but also that the distance between neighbouring methyl groups in neighbouring layers is 4·16 Å., exactly the distance found in methane but greater than that in durene, 3·81 Å.

Trimethylplatinum chloride is found by E. G. Cox and K. C. Webster [1] to crystallise in the cubic system and to have a trigonal axis of symmetry. The four platinum valencies for this type of binding cannot be coplanar. Diamminosilver groups in

$$[Ag(NH_3)_2]_2SO_4\ {}^2 \text{ and } [Ag(NH_3)_2]NO_3\ {}^3$$

are probably linear, and the $Cd(NH_3)_4$ groups in $Cd(NH_3)_4(ReO_4)_2$ [4] are tetrahedral.

A large number of workers have been concerned to show by *X*-ray methods whether the 4-co-ordination compounds of nickel, palladium, platinum, and copper are tetrahedral or planar; except the trimethyl compound, all are found to be planar. The clearest structure is that of $[Pd(NH_3)_4]Cl_2,H_2O$, studied by B. N. Dickinson.[5] The $Pd(NH_3)_4$ groups lie in planes 4·3 Å. apart, which are separated by chlorine ions with the water groups in the interstices of the structure. The Pd–N distance is found to be 2·02 Å. and the group is strictly tetragonal.

An elaborate study has been made of $(NH_4)_2CuCl_4,2H_2O$ by L. Chrobak [6] to clear up disputes that had existed as to its nature.

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[96] J. L. Hoard and L. Goldstein, *J. Chem. Physics*, 1935, **3**, 117.

[97] *Proc. Roy. Soc.*, 1934, [*A*], **144**, 75; *A.*, 1934, 479; see also J. D. H. Donnay and J. Mélon, *Proc. Nat. Acad. Sci.*, 1934, **20**, 327; *A.*, 1934, 947; J. W. Illingworth and J. F. Keggin, *J.*, 1935, 575; *A.*, 834; J. A. Santos, *Proc. Roy. Soc.*, 1935, [*A*], **150**, 309; O. Kraus, *Z. Krist.*, 1935, **91**, 402.

[98] See *Ann. Reports*, 1933, **30**, 409.

[99] *Z. Krist.*, 1934, **87**, 370; *A.*, 1934, 479.

[1] *Ibid.*, 1935, **90**, 561.

[2] R. B. Corey and R. W. G. Wyckoff, *ibid.*, 1934, **87**, 264; *A.*, 1934, 352.

[3] R. B. Corey and K. Petrescov, *ibid.*, 1935, **89**, 528.

[4] K. S. Pilzer, *ibid.*, **92**, 131.

[5] *Ibid.*, 1934, **88**, 281; *A.*, 1934, 1161.

[6] *Ibid.*, p. 35; *A.*, 1934, 1060.

A planar arrangement is found for the four chlorine atoms, though they turn out to be at different distances—2·0 and 2·35 Å.—from the copper atom. The water molecules here are, however, co-ordinated at a distance of 2·0 Å. from the copper. E. G. Cox, W. Wardlaw, and K. C. Webster [7] have studied a number of other complex derivatives of palladium, platinum, nickel and copper. The most convincing evidence is obtained from the dithio-oxalate derivatives of the first three metals, which crystallise with the whole of the complex in planes separated by a distance of 5·5 Å. apart and have diad axes of symmetry. Similar evidence is provided by salicylaldoxime and other complexes of these metals, all of which crystallise with the complex molecules in layers 4 Å. apart, excluding any possibility of tetrahedral arrangement.

Similar results have been found for palladium chloride, oxalate, and chloro-dinitrite,[8] but is was impossible to analyse the simple compound $PdCl_2(NH_3)_2$ on account of its forming a two-dimensional lattice of a statistical kind (see p. 188).

A study showing a complete isomorphism between the tetracyanide salts of nickel, palladium, and platinum and one less complete between those of Mg, V and Er has been made by H. Brasseur and his collaborators.[9] The complex has a centre of symmetry and therefore must have a planar configuration. On the other hand, in Cs_3CoCl_5 studied by H. M. Powell and A. F. Wells [10] the complex $CoCl_4$ seems to exist as a regular tetrahedron, the remaining Cl ion occupying a different place in the structure.

Of the hexa-co-ordinated compounds an interesting example is given by $[Rh(NH_3)_5Cl]Cl_2$.[11] The complex ions are slightly distorted octahedra, held together by the free chlorine ions. Nickel nitrites [12] and cæsium aurichlorides [13] have also been studied.

Hydrated Salts.—Recent detailed studies of hydrated salts have brought out the function of water of crystallisation much more clearly. Water is found, in general, either attached to a positive ion, or lying between other water molecules and negative ions. In either case the arrangement of the water molecule is such as to satisfy the binding properties postulated by the Bernal–Fowler theory.[14] In the first case the ion may occupy one or two of the positions of negative attraction in the molecule ion, according to its polarising power. The degree of binding of the water is shown very clearly by its infra-red absorption,[15] which varies from that of ice to that of water according to the tightness with which the molecule is held. Lithium sulphide monohydrate is the only example of a monohydrate studied.[16] Each water molecule is attached to one lithium atom, to two sulphate oxygens, and to another water molecule. The binding is so slight, $H_2O–H_2O = 2{\cdot}86$ Å., that rotation of groups is not excluded. The crystal structure of $CuSO_4,5H_2O$, which has been completely worked out by C. A. Beevers and H. Lipson,[17] is of particular interest to chemists. The five water molecules are differently situated; four are arranged in a plane about the copper atoms at a distance of 1·97—2·0 Å., and the other is not attached to any metal atom but connected tetrahedrally to two water molecules of the first type and two sulphate oxygens. The copper group also contains two sulphate oxygens, but at a greater distance, 2·3, 2·45 Å., so there is no doubt that water molecules are here held by planar co-ordination forces. The whole structure satisfies very exactly Pauling's ionic valency scheme. C. A. Beevers and C. M. Schwartz [18] have examined $NiSO_4,7H_2O$, and here again six of the water molecules are co-ordinated to the nickel and one is loose.

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[7] *J.*, 1935, 731, 1475; see also F. W. Pinkard, E. Sharratt, W. Wardlaw, and (in part) E. G. Cox, *J.*, 1934, 1012; *A.*, 1934, 994; E. G. Cox, H. Saenger, and W. Wardlaw, *ibid.*, p. 182; *A.*, 1934, 397.

[8] F. G. Mann, (Miss) D. M. Crowfoot, D. C. Gattiker, and (Mrs.) N. Wooster, *J.*, 1935, 1642.

[9] J. Piérard and A. de Rassenfosse, *Z. Krist.*, 1935, **90**, 470; A. de Rassenfosse and J. Piérard, *Bull. Soc. Sci. Liège*, 1935, 74; H. Brasseur and A. de Rassenfosse, *ibid.*, pp. 24, 68, 171, 277; H. Brasseur, A. de Rassenfosse, and J. Piérard, *Compt. rend.*, 1934, **198**, 1048; *A.*, 1934, 479.

[10] *J.*, 1935, 359.

[11] C. D. West, *Z. Krist.*, 1935, **91**, 181.

[12] A. Ferrari and C. Colla, *Gazzetta*, 1935, **65**, 168, 789, 809; A. Ferrari, A. Baroni, and C. Colla, *ibid.*, p. 797.

[13] N. Elliott, *J. Chem. Physics*, 1934, **2**, 419; *A.*, 1934, 947.

In the hexahydrates of magnesium and aluminium halides, an almost regular octahedral co-ordination of water molecules round the cations is found.[19] Some curious isomorphous relations have been found by C. D. West [20] in the hydrates of perchlorates and iodides. In the first place, iodine and perchlorate ions seem to function almost identically in the structure owing to high symmetry, not to rotation. In the second place, $Ba(ClO_4)_2,3H_2O$ is found to be isomorphous with $LiClO_4,3H_2O$.

A very complete study of the alums $M^{III}6H_2O,M^{I}(SO_4)_26H_2O$ has been made by H. Lipson.[21] Three types of alum structure have been found, corresponding to (i) very large univalent ions, *e.g.*, Cs,$N(CH_3)_4$; (ii) medium-sized ions, Rb,K; and (iii) small ions, Na. All alums have in common the co-ordination of six water molecules round the tervalent cation. The first two differ in the arrangement of the remaining six water molecules, and sodium alum has the reverse position of the sulphate group along the trigonal axis. As all three are cubic structures, we have here a case where only *X*-rays can show that the series is not isomorphous.

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[14] See *Ann. Reports*, 1934, **31**, 42.

[15] L. Passerini, *Gazzetta*, 1935, **65**, 502, 511; *A.*, 1300.

[16] G. E. Ziegler, *Z. Krist.*, 1934, **89**, 456.

[17] *Nature*, 1934, **133**, 214; *A.*, 1934, 243; *Proc. Roy. Soc.*, 1934, [*A*], **146**, 570.

[18] *Z. Krist.*, 1935, **91**, 157.

[19] K. R. Andress and J. Gundermann, *ibid.*, 1934, **87**, 345; *A.*, 1934, 479; K. R. Andress and C. Carpenter, *ibid.*, p. 446; *A.*, 1934, 947.

[20] *Ibid.*, **88**, 198; *A.*, 1934, 1161; *ibid.*, 1935, **91**, 480.

[21] *Phil. Mag.*, 1935, **19**, 887; *Proc. Roy. Soc.*, 1935, [*A*], **151**, 347; *A.*, 1308; H. Lipson and C. A. Beevers, *ibid.*, **148**, 664.

The only complete study of a salt containing molecules, other than water and ammonia, has been made by S. B. Hendricks for $CaSO_4,4CO(NH_2)_2$.[22] The urea groups act as dipole links between the positive and negative ions of the salt. $AgNO_3,CO(NH_2)_2$ has probably a similar structure.[23]

J. D. B.
A. F. W.

MOLECULAR CRYSTALS.

Last year some of the most important advances described in the report were those resulting from the application of rapid preliminary measurements and extensive surveys of related substances to the structure of unknown chemical compounds. Such was the work on the sterols, sex hormones, and related compounds which has continued to yield valuable results.[1] This method depends upon the use of optical or magnetic measurements to determine the probable orientation of the molecules in the crystal, and upon the use of molecular models derived from the results of exact structure determinations.

Considerable doubt has been expressed in the past as to the absolute reliability of the first of these methods, and it is therefore particularly satisfactory that we now have several examples in which exact structure determinations have confirmed the molecular orientations chosen from optical and magnetic data.[2] Further, a very complete test has been applied to the whole theory by S. B. Hendricks and W. E. Derning[3] from an examination of the optical anisotropy of the crystals of a series of oxalates. They have calculated the birefringences of the crystals from the molecular refractivities and the orientations of the molecules in the crystal previously deduced from X-ray data. There is very close agreement between the calculated and observed birefringences, which indicates that no confusion is caused by intermolecular interaction. Similar calculations have been made with good results for guanidinium iodide[4] and for sodium carbonate monohydrate.[5] The usefulness of even the molecular refractivities calculated direct from the crystal refractive indices as an indication of molecular structure has been demonstrated by A. Neuhaus[6] for a large series of compounds.

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[22] *J. Physical Chem.*, 1933, **37**, 1109; *A.*, 1934, 243.

[23] G. L. Clark and C. O. Werner, *Z. Krist.*, 1934, **88**, 162; *A.*, 1934, 1162.

[1] G. E. R. Schulze, *Z. physikal. Chem.*, 1934, [*A*], **171**, 436; Y. Go and O. Kratky, *ibid.*, [*B*], **26**, 439; J. D. Bernal and (Miss) D. M. Crowfoot, *Chem. and Ind.*, 1934, **53**, 953; *A.*, 1934, 1354; 1935, **54**, 701; *A.*, 1120; D. M. Crowfoot, *ibid.*, p. 568; A. Kofler and A. Hauschild, *Z. physiol. Chem.*, 1934, **224**, 150; *A.*, 1934, 815; S. B. Hendricks, *Z. Krist.*, 1934, **89**, 427; *A.*, 1935, 152; A. Neuhaus, *ibid.*, **89**, 505; *A.*, 1934, 413; *ibid.*, 1935, **90**, 415; *A.*, 1195; H. Brasseur, *ibid.*, **91**, 369; G. Mackinney, *J. Amer. Chem. Soc.*, 1934, **56**, 488; *A.*, 1934, 352.

[2] K. S. Krishnan and S. Banerjee, *Proc. Roy. Soc.*, 1935, **234**, 265.

[3] *Z. Krist.*, 1935, **91**, 290.

Still more important advances have been made in the direction of exact structure determination, and it is in this field that we have most interesting results to report. Last year we listed the interatomic distances found in seven organic crystals of which complete structure analyses had been made up to that date, but this list could now be more than doubled. A very good summary of the extent to which interatomic distances had been measured with precision by X-rays up to the end of 1934 has been given by J. M. Robertson.[7] Another list also appears in a paper by H. Mark[8] which supplies in addition a valuable survey of the various physical methods available for the study of the shape and structure of organic molecules.

The first Fourier analyses of organic compounds, such as those of urea, thiourea, naphthalene, and anthracene, did little more than render precise the pictures of the structures already accepted by organic chemists through the attachment of these exact interatomic distances. But the last two years have seen the extension of the method into the field of pure chemistry in two directions. The first is the direct determination of the mutual orientation of the constituent atoms where this is unknown, as in the case of cyanuric triazide (see below). The second is a determination of the nature of the chemical bonds present. The measurements of standard organic compounds have provided us with a scale of bond lengths, normal distances between atoms both inter- and intra-molecular, to be applied to actual substances under investigation. But the results obtained by the application of this scale are rapidly leading us beyond the pictures of molecular structure given us by classical organic chemistry.

Simple Molecular Structures.—Considerable work has been done by improved techniques in the examination of crystals at low temperatures. L. Vegard[9] has determined the structures of α-(fixed) and β-(rotating) nitrogen, and shown that those of carbon monoxide are almost exactly similar.[10] The C–O distance in solid carbon dioxide is found to be 1·13 ± 0·02 Å.[11] The structure of oxygen in its different forms has been very much studied, but no conclusive results have been obtained. Absorption-spectrum studies [12] point to the existence of O_4 molecules in liquid oxygen and in all forms of solid oxygen. Vegard [13] has shown that γ (high-temperature) oxygen has a cubic structure $a = 6{\cdot}83$ Å. containing 16 atoms and consequently almost certainly four rotating molecules of O_4. These must lie along the trigonal axes, and consequently a structure such as (I) is more probable than (II); α- and β-oxygen

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[4] W. Theilacker, *Z. Krist.*, 1935, **91**, 90.

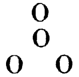
[5] H. Brasseur, *ibid.*, p. 282.

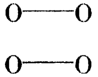
[6] *Ber.*, 1934, **67**, 1627.

[7] *Phys. Soc. Rep.*, p. 46; *Chem. Rev.*, 1935, **16**, 417.

[8] *Z. Elektrochem.*, 1934, **40**, 413; *A.*, 1934, 1088.

(I.)



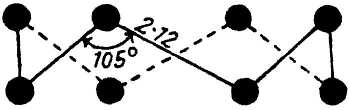


(II.)

have very similar structures, but they are rhombohedral and not cubic and contain three molecules of O_4.

E. F. Burton and W. F. Oliver [14] have shown that water vapour condensed at temperatures below − 110° gives rise, not to ice, but to water glass, which, to judge from the position of the intensity maxima, must have a density equal to or less than that of ice at the same temperature. At − 110° this water glass rapidly devitrifies to ordinary ice. Solid hydrogen peroxide [15] is found to have a tetragonal structure, $c = 8{\cdot}02$, $a = 4{\cdot}02$, with four molecules per cell. The arrangement may be similar to that of cristobalite.

FIG. 5.



Molecule of Sulphur S_8.

The structure of two forms of sulphur has been determined. A careful study of rhombic sulphur by A. E. Warren and J. T. Burwell [16] has shown that the cell contains 16 molecules of S_8; these molecules are in the form of puckered octagons (see Fig. 5), with an S–S distance of 2·12 Å. (calc., 2·16) and a bond angle of 105·4°. The S_8 molecules are stacked in four layers approximately perpendicular alternately to the (110) and $(1\bar{1}0)$ directions in the cell; the nearest approach between sulphur atoms in neighbouring molecules is 3·3 Å. Plastic sulphur is the simplest type of polymerised fibre structure. On stretching, it can, like rubber, be made to crystallise, though normally it is amorphous: that is, the sulphur chains are tangled with each other. The structure that these fibres form has been thoroughly worked out by K. H. Meyer and Y. Go;[17] the cell is monoclinic with an identity period of 9·26 Å. along the fibre axis. A close analogy to the polymorphism of sulphur is furnished by $(PCl_2N)_x$ which forms both 3- and 6-unit rings[18] and also elastic polymerised fibres of period 5·16 Å.[19] Partial studies have been made of two red monoclinic varieties of selenium[20] which also probably contain Se_8 molecules.

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[9] *Proc. K. Akad. Wetensch. Amsterdam*, 1934, **37**, 780; *A.*, 1935, 147.

[10] *Z. Physik*, 1934, **88**, 235; *A.*, 1934, 587.

[11] W. H. Keesom and J. W. L. Köhler, *Physica*, 1934, **1**, 167; *A.*, 1934, 244.

[12] A. Prichotko, M. Ruhemann, and A. Federitenko, *Physikal. Z. Sovietunion*, 1935, **7**, 410; *A.*, 1291; M. Guillien, *Compt. rend.*, 1934, **198**, 1486; *A.*, 1934, 581; H. Salow, *Z. Physik*, 1934, **90**, 11; *A.*, 1934, 1055; W. Finkelnburg, *ibid.*, p. 1; *A.*, 1934, 1055.

[13] *Ibid.*, 1935, **98**, 1.

[14] *Proc. Roy. Soc.*, 1935, [*A*], **153**, 166.

[15] F. Feher and F. Klötzer, *Z. Elektrochem.*, 1935, **41**, 850.

[16] *J. Chem. Physics*, 1935, **3**, 6.

The structure of red and black phosphorus has been studied by R. Hultgren, N. S. Gingrich, and B. E. Warren.[21] The amorphous form of both has been analysed and shows a layer lattice of 3-co-ordination type not unlike that of graphite with an internuclear distance of 2·28 Å. The crystalline form, on the other hand, is a new type of structure and, like arsenic, of the layer type, with 3-co-ordination but with a rhombic type of trigonal layers. The atoms in the layers are 2·18 Å. apart (calc., 2·20 Å.). The atoms in different layers are separated by 3·68 Å.

Molecules of the symmetrical types AB_4, AB_6, generally form simple crystal structures. Exceptions to this rule are ZrF_4 and HfF_4 which give monoclinic crystals.[22] Pentaerythritol tetraphenyl ether, on the other hand, has a simple tetragonal cell with $a = 12{\cdot}32$, $c = 8{\cdot}43$ Å., with alternating tetragonal symmetry and two molecules in the unit cell.[23] This is very similar to tetraphenylmethane,[24] which is also tetragonal, $a = 10{\cdot}86$, $c = 7{\cdot}26$ Å., differing only in the smaller axes and in the fact that here the molecule also possesses planes of symmetry. Hexamethylethane and hexachloroethane,[25] above − 125° and 71° respectively, are cubic body-centred structures, again with only two molecules in the cell, due presumably to molecular rotation. Of the less symmetrical disubstituted ethane derivatives, *s*-di-iodoethane[26] shows a considerably more complicated packing. The molecules do not rotate about the C–C bond at ordinary temperatures, and it is interesting that the position taken up by the iodine atoms with respect to one another is the same as that in *s*-di-iodoethylene, *viz.*, the *trans*-position. The crystals of these two compounds are very closely isomorphous.

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[17] *Helv. Chim. Acta*, 1934, **17**, 1081.

[18] P. Renaud, *Ann. Chim.*, 1935, [xi], **3**, 443; *A.*, 833; *Compt. rend.*, 1934, **198**, 1159; *A.*, 1934, 615.

[19] *Arch. Sci. phys. nat.*, 1935, **17**, supp. 139; *Trans. Faraday Soc.*, 1936, **32**, 148.

[20] H. P. Klug, *Z. Krist.*, 1934, **88**, 128; *A.*, 1934, 1160.

[21] *J. Chem. Physics*, 1935, **3**, 351.

[22] G. E. Schulze, *Z. Krist.*, 1934, **89**, 477.

[23] J. Beintema, P. Terpstra, and W. J. van Weerden, *Rec. trav. chim.*, 1935, **44**, 627; *A.*, 1195.

[24] W. H. George, *Proc. Roy. Soc.*, 1926, [*A*], **113**, 585.

[25] C. D. West, *Z. Krist.*, 1934, **88**, 195; *A.*, 1934, 1162.

Aliphatic Compounds.—Among the main group of aliphatic compounds exact structure determinations are still very rare. We have still no Fourier analysis of aliphatic long chains, though a beginning has been made by D. A. Wilson and E. Ott[27] towards the calculation of the intensities of the main plane reflexions of a series of aliphatic alcohols. Otherwise, work in this field is mainly confined in usefulness to the identification of products from natural sources[28] together with preliminary studies on the structure of dibasic acids,[29] triglycerides,[30] and dihydrazides.[31] In the series of the polymethylene ring compounds[32] the interesting fact emerges that, whereas at ordinary temperatures and in the liquid the molecular volume of a methylene group is greater in the cyclic than in the straight-chain compounds, yet this difference disappears at low temperatures.

The only complete structure determinations in the aliphatic series are those of hexamethylenetetramine and urea, which have been further refined by R. W. G. Wyckoff and R. B. Corey.[33] Their results give valuable new readings for the *F* curves of carbon and nitrogen in this type of compound, and also lead to slightly different values for the interatomic distances. In hexamethylenetetramine, CH_2–N = 1·42 Å., while in urea, C=O = 1·25 and C–NH_2 = 1·37 Å. The shortening of the distance of C–N in urea from 1·42 to 1·37 Å. is of particular interest, since here resonance may occur between the two forms $\genfrac{}{}{0pt}{}{H_2N}{H_2N}\!>\!C{=}O$ and $\genfrac{}{}{0pt}{}{HN}{H_2N}\!>\!C{-}OH$, the former predominating.

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[26] H. P. Klug, *J. Chem. Physics*, 1935, **3**, 747 ; *Z. Krist.*, 1935, **90**, 495 ; *A.*, 1195.

[27] *J. Chem. Physics*, 1934, **2**, 231, 239; *A.*, 1934, 720.

[28] F. J. E. Collins, *J. Soc. Chem. Ind.*, 1935, **54**, 33; S. H. Piper, A. C. Chibnall, and E. F. Williams, *Biochem. J.*, 1934, **28**, 2175; A. C. Chibnall, S. H. Piper, A. Pollard, E. F. Williams, and P. N. Sahai, *ibid.*, p. 2189; A. C. Chibnall and S. H. Piper, *ibid.*, p. 2209; *A.*, 1935, 551, 152, 267, 204.

[29] F. D. La Tour and A. Riedberger, *Compt. rend.*, 1934, **199**, 215; *A.*, 1934, 1060; F. D. La Tour, *ibid.*, 1935, **201**, 479; *A.*, 1351.

[30] C. E. Clarkson and T. Malkin, *J.*, 1934, 666; *A.*, 1934, 720.

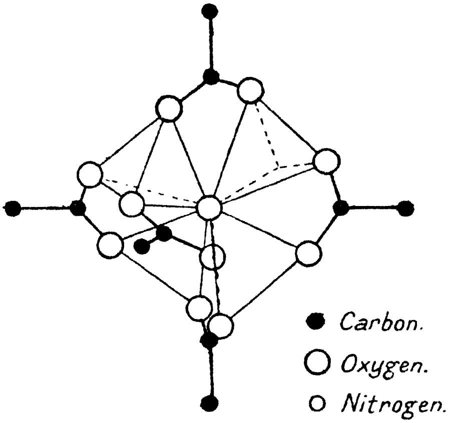
[31] M. Wolf, *Physica*, 1934, **1**, 417; *A.*, 1934, 587.

[32] A. Müller, *Nature*, 1935, **135**, 994; *A.*, 957.

[33] *Z. Krist.*, 1934, **89**, 462; cf. R. Reinicke, *ibid.*, 1935, **87**, 417.

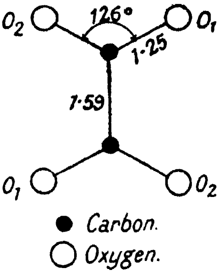
In the guanidinium halides investigated by W. Theilacker,[34] the distance C–N is still more reduced, the value given being 1·18 Å., although the measurement is not susceptible of great accuracy. Theilacker has studied the chloride, bromide, and iodide, but only for the last could the crystal structure be determined with any approach to precision. This forms a typical layer lattice with iodine ions arranged on a network of puckered hexagonal rings separated by guanidine ions. The guanidinium ion $C(NH_2)_3$ shows trigonal symmetry, all three nitrogen atoms being crystallographically equivalent, and the ionic character cannot therefore be associated with any particular nitrogen atom of the complex. The structure may be written as (I) with a positive charge on the carbon, or as due to resonance between three double-bonded structures of the type (II).

FIG. 6.



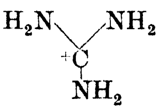
The molecule $Be_4O(CH_3{\cdot}COO)_6$ (*one acetate group is omitted*).

FIG. 7.



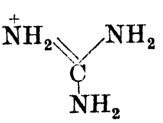
The oxalate-ion.

(I.)



$$H_2N-\overset{+}{C}(-NH_2)-NH_2$$

(II.)



$$\overset{+}{N}H_2{=}C(-NH_2)-NH_2$$

Considerable interest has centred round another " resonance " problem, *viz.*, the structure of the carboxyl group, and several studies have been made of carboxylic acids and their salts.[35] Besides the electron diffraction of formic acid[36] reported last year, Pauling has examined the crystal structure of basic beryllium acetate.[37] Here he finds actual molecules $Be_4O(CH_3{\cdot}COO)_6$ present in the crystal and packed together as are the atoms in diamond. Inside the molecules (Fig. 6) each beryllium atom is at the centre of a tetrahedron formed by three oxygen atoms contributed by acetate groups and the central basic oxygen. The interatomic distances have not been determined with any great accuracy, but Pauling can detect, as in formic acid, no difference between the two oxygen atoms of the carboxyl group. He gives the C–O distance as 1·29 ± 0·05 Å. and the O–C–O angle as 124° ± 3°.

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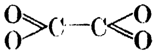
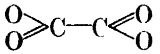
[34] *Z. Krist.*, 1935, **90**, 51, 256; cf. A. Swaryczewski, *Bull. Acad. polonaise*, 1933, [*A*], 359; *A.*, 1934, 587; *ibid.*, 1934, [*A*], 246; *A.*, 1935, 152.

[35] L. P. Biefield and P. M. Harris, *J. Amer. Chem. Soc.*, 1935, **57**, 396; E. Hertel and G. H. Römer, *Z. physikal. Chem.*, 1934, [*B*], **27** 282; *A.*, 1935, 152; R. C. Evans, *Z. Krist.*, 1935, **92**, 154.

A somewhat more exact determination of the configuration of the carboxyl group has been made by W. H. Zachariasen[38] in his analysis of the structure of oxalic acid dihydrate, and this has been confirmed by S. B. Hendricks for other oxalates.[39] Zachariasen finds for the oxalate group a planar configuration with a centre of symmetry (Fig. 7). The C–C distance is 1·59 ± 0·07 Å., C–O in both cases 1·25 ± 0·05 Å., and the O–C–O angle 126°. The two oxygen atoms are not, however, structurally identical, and their arrangement with respect to the water molecules in the crystal is different. Since the distances between the oxygen atoms in the oxalate groups and water molecules are only 2·87, 2·77, and 2·60 Å., considerably shorter than the usual intramolecular distance of 3·5 Å., Zachariasen has suggested that the water molecules bind the oxalate groups in chains by a series of hydrogen bonds. Later, J. D. Bernal and (Miss) H. D. Megaw[40] showed that there are two possible ways of achieving this binding through two different systems of combined hydrogen and hydroxyl bonds according to whether O_1 or O_2 is acting as hydroxyl group. The interconversion of the two systems is effected by the movement of hydrogen atoms along the oxygen chains, and this movement provides a mechanism for the resonance of the two forms :



$$\begin{matrix}O\\O\end{matrix}\!\!\begin{matrix}=\\-\end{matrix}\!\!C-C\!\!\begin{matrix}-\\=\end{matrix}\!\!\begin{matrix}O\\O\end{matrix}$$



$$\begin{matrix}O\\O\end{matrix}\!\!\begin{matrix}-\\=\end{matrix}\!\!C-C\!\!\begin{matrix}=\\-\end{matrix}\!\!\begin{matrix}O\\O\end{matrix}$$

It does seem, however, that resonance may not be complete, and the limits of error of Zachariasen's measurement leave still open the possibility of comparatively small differences in the $C–O_1$ and $C–O_2$ distances.

Aromatic Compounds.—In the aromatic series a number of new and very important structure analyses have been carried out. The simplest of these is resorcinol,[41] of which only a preliminary report is available. Here the benzene ring appears regular, with a C–C distance 1·41 Å., and C–OH 1·35 Å. The molecules are arranged in spiral formation about the diad screw axis in such a way that hydroxyl groups in neighbouring molecules are brought to within a distance of 2·66—2·76 Å. of one another. This close approach indicates binding between the hydroxyl groups of the kind discussed above with reference to oxalic acid and also among inorganic compounds. Such association between hydroxyl groups has long been recognised in organic chemistry, but these measurements provide the first accurate description of the nature of the binding.

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[36] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sci.*, 1934, **20**, 336.

[37] L. Pauling and J. Sherman, *ibid.*, p. 340.

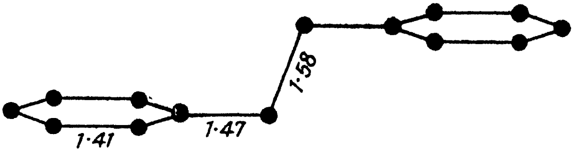
[38] *Z. Krist.*, 1934, **89**, 442; *A.*, 1935, 152; *Physical Rev.*, 1934, **45**, 755.

[39] *Z. Krist.*, 1935, **91**, 48.

[40] *Proc. Roy. Soc.*, 1935, [*A*], **151**, 384.

Research has been continued on several compounds based on condensed ring systems. The complete analysis of chrysene[42] is of particular interest as a control to the work undertaken on hydrocarbons related to the sterols.[43] Preliminary measurements are also reported for 1 : 2-*cyclo*pentenophenanthrene[44] and for dodecahydrobenzanthracene[45] which shows, as would be expected, a considerable thickening of the molecule, and also of the optical and magnetic properties of 1 : 2 : 5 : 6-dibenzanthracene.[46] 1 : 3 : 5-Triphenylbenzene[47] is closely related in crystallographic behaviour to the condensed-ring compounds, since the molecules appear perfectly flat with all the phenyl rings extended symmetrically coplanar with the central ring. In the crystals, they are packed closely interlocking in layers, with the molecular planes very slightly inclined to the normal to a pseudotrigonal axis.

FIG. 8.



Dibenzyl.

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[41] J. M. Robertson, *Z. Krist.*, 1934, **89**, 318; *Nature*, 1935, **136**, 755.

[42] J. Iball, *Proc. Roy. Soc.*, 1934, [*A*], **146**, 140; *A.*, 1934, 1162.

[43] J. D. Bernal and (Miss) D. M. Crowfoot, *J.*, 1935, 93.

[44] J. Iball, *Z. Krist.*, 1935, **92**, 293.

[45] *Idem, Chem. and Ind.*, 1935, **54**, 716.

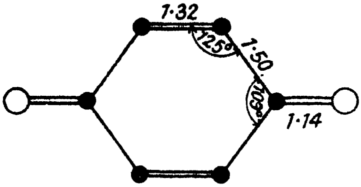
[46] J. Iball and J. M. Robertson, *Nature*, 1933, **132**, 750; *A.*, 1934, 17; J. D. Bernal, *ibid.*, p. 751; *A.*, 1934, 18; K. S. Krishnan and S. Banerjee, *Z. Krist.*, 1935, **91**, 170, 173.

[47] B. P. Orelkin, *J. Gen. Chem. Russia*, 1933, **3**, 643; *A.*, 1934, 134; (Mrs.) K. Lonsdale, *Nature*, 1934, **133**, 67; *A.*, 1934, 134; B. Orelkin and (Mrs.) K. Lonsdale, *Proc. Roy. Soc.*, 1934, [*A*], **144**, 630; *A.*, 1934, 834; K. S. Krishnan and S. Banerjee, *Nature*, 1934, **133**, 497; *A.*, 1934, 479.

In dibenzyl, on the other hand, in contrast with the arrangement in triphenylbenzene and also in diphenyl, the two benzene rings are no longer coplanar. Preliminary examination by J. Dhar[48] suggested a molecule only slightly distorted from the coplanar structure, but the complete analysis by J. M. Robertson[49] shows clearly that the planes of the benzene rings are directly at right angles to the zigzag of the CH_2 groups (Fig. 8). Between the aliphatic and aromatic carbon atoms the distance is 1·47 Å., and between the two CH_2 groups it is 1·58 Å. The angle between the bonds of the CH_2 groups is 109·2—112°.

In all the compounds so far considered, the benzene rings appear as perfectly regular hexagons with a distance between the carbon atoms of 1·41 Å. In benzoquinone, chemical theory would expect considerable distortion from this model, and this has been found to be the case.[50] Owing to the orientation of the molecules in the crystal, their dimensions cannot be obtained from the Fourier analysis with such accuracy as in other examples. But there does appear to be definite lengthening of the C–C bonds adjacent to the C=O group to 1·50 Å., and shortening of the ring bonds parallel to this to 1·32 Å., corresponding to the appearance of aliphatic single and double bonds (Fig. 9). The C=O distance appears smaller than might be expected, 1·14 Å., but this agrees with the C=O distance of 1·16 Å. found in carbon dioxide from the infra-red absorption spectrum and 1·13 Å. from crystal-structure data at low temperatures (p. 225). It may be compared with the C=O distance of 1·25 Å. found for urea and oxalic acid, and in so far, it confirms that the latter are midway between 'true' single and double bonds.

FIG. 9.



Benzoquinone.

This distortion of the benzoquinone molecule is, at least in its direction, in accordance with current chemical theory. But nearly as far-reaching changes of an altogether unexpected kind have been found by R. W. James, G. King, and H. Horrocks in *p*-dinitrobenzene.[51] A preliminary examination of this compound, carried out by K. Banerjee,[52] gave results roughly in agreement with the stereochemical picture presented by the ordinary chemical formula. The exact structure obtained by James by Fourier projections on three planes reveals important departures from this picture which are best shown by reference to Fig. 10. The molecule as a whole possesses a centre of symmetry. The nitro-group is nearly planar, but apparently not quite, and nearly coplanar with the benzene ring, one oxygen atom being in this plane and the second slightly lifted above it. The distance between the carbon atom of the ring and the nitrogen atom is 1·53 Å., decidedly longer than the C–N distance of hexamethylenetetramine. Further, the two oxygen atoms are at different distances from the nitrogen, *viz.*, 1·10 and 1·25 Å. These might correspond to distances between $N{=}O$ and $N \rightarrow O$ in the usually written structure of the nitro-group $-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$, though both are actually shorter than the accepted distances, *viz.*, for $N{=}O$, 1·22 Å., and for $N \rightarrow O$, 1·36 Å.[53] It is surprising, however, that any difference should exist between them at all, since the resonance energy between the two equivalent configurations is considerable. Very careful measurements by H. O. Jenkins[54] have shown that *p*-dinitrobenzene has no dipole moment, and this has been taken to prove that the oxygen atoms of the nitro-group are equivalent. The only alternative is to assume that the exact configuration shown to exist in the solid state, which has a centre of

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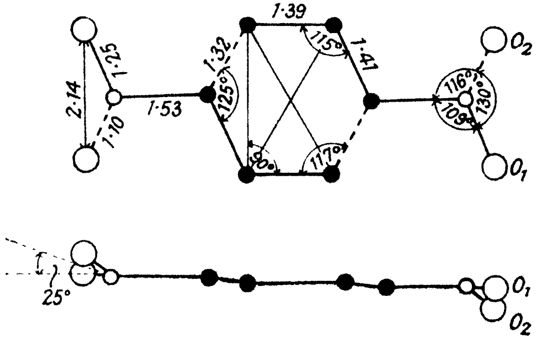
[48] *Current Sci.*, 1934, **2**, 480; *A.*, 1934, 948.

[49] *Proc. Roy. Soc.*, 1934, **146**, 473; 1935, **150**, 348.

[50] *Ibid.*, p. 106; *Nature*, 1934, **134**, 138; *A.*, 1934, 948.

FIG. 10.



p-*Dinitrobenzene.*

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[51] *Proc. Roy. Soc.*, 1935, **153**, 225.

[52] *Phil. Mag.*, 1934, **18**, 1004.

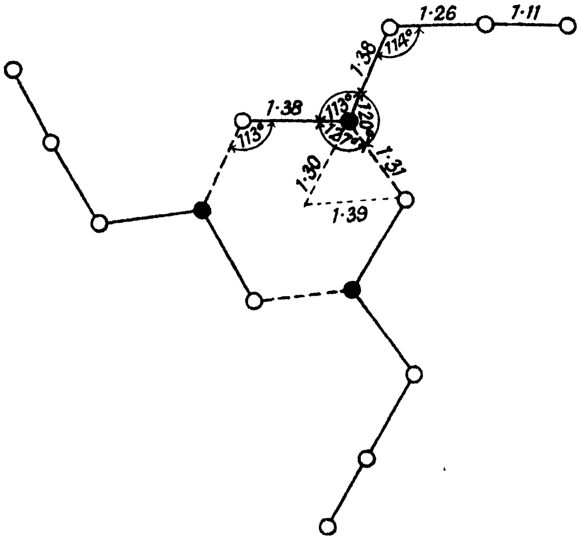
[53] N. V. Sidgwick, *Ann. Reports*, 1934, **31**, 39.

[54] *Nature*, 1934, **134**, 217.

symmetry, is also that present in solution, *i.e.*, that there is no free rotation about the C–N bond.

Perhaps one fact in support of this hypothesis is the very marked interaction that appears to occur between the nitro-group and the benzene nucleus. The substitution of the nitro-group has produced a considerable shortening of one of the bonds in the ring adjacent to it—that approximately parallel to the shorter N=O bond—though there is no compensatory lengthening of other nuclear bonds. The configuration of the ring as a whole can be regarded as tending towards one of the Dewar types of canonical structure which in benzene itself is probably only present to the extent of about 7·3% (Pauling and Wheland).[55] But we have evidently to deal here with a process which it is practically impossible to discuss in terms of ordinary valency changes. It would be most interesting if this striking modification in shape of the benzene nucleus produced by the substitution in it of nitro-groups could be related to the general phenomenon of the influence of substituents on the reactivity of the benzene nucleus.

FIG. 11.



Cyanuric triazide.

More information in the same direction is given by the determination of the crystal structure of cyanuric triazide, one of the most important and elegant pieces of work accomplished in the last two years.

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[55] *J. Chem. Physics*, 1933, **1**, 362.

Two parallel investigations have been undertaken. That of E. A. Hughes [56] leads to a structure agreeing within the limits of his own experimental accuracy with that of (Miss) I. Knaggs,[57] although it makes no pretensions to such perfection. It is, however, of some interest in indicating how far merely visual estimates of intensities may be relied on to give a very good first approximation picture of a complex structure. Miss Knaggs has made very accurate intensity measurements and converted these into an absolute scale by comparison with standard crystals both by ionisation and photographic methods. The results of her analysis lead to the structure of the cyanuric triazide molecule shown in Fig. 11. The molecule as a whole is planar, with a trigonal axis perpendicular to the plane. The azide group is attached to the carbon atom of the ring and is proved to be linear, the possible deviation from the straight line being not more than 4°. It is, however, not centrosymmetrical, the distance between the nitrogen attached to the ring and the central nitrogen atom being 1·26 Å., while that between the two outer nitrogen atoms is 1·11 Å. This is in good agreement with the suggestion of N. V. Sidgwick [58] that the actual structure is the result of resonance between $-\mathrm{N}{=}\mathrm{N}\Rightarrow\mathrm{N}$ and $-\mathrm{N}\leftarrow\mathrm{N}{\equiv}\mathrm{N}$.

The ring itself is considerably distorted from the hexagonal shape. It consists of alternate carbon and nitrogen atoms whose distances are alternately 1·31 and 1·39 Å. apart. Both these distances are shorter than C–N of hexamethylenetetramine, but as a first approximation they may be attributed to alternate double and single links. We must assume that, in contrast to benzene itself, one of the two Kekulé forms is frozen in cyanuric triazide by the unsymmetrical form of the azide substituent, just as in *p*-dinitrobenzene another of the canonical structures appears forced on the molecule.

A number of other investigations of aromatic compounds are still in a preliminary stage.[59] That of W. H. Taylor on methylene-blue halides [60] is interesting in showing that the packing of organic ions in a crystal follows much the same principles as that of inorganic ions. The iodide ion in methylene-blue iodide, for example, does not appear to be associated particularly with any special part of the C–N–S chain but is packed conveniently between the ends of the lath-shaped molecules. A still more complicated molecular type is that of the phthalocyanines, where investigation proves the presence of approximately square flat molecules having a centre of symmetry.[61] This centre may be either left empty or occupied by the metals nickel, copper, or platinum without distortion of the crystal lattice, and in all these cases the four valencies of the metals must be coplanar.

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[56] *J. Chem. Physics*, 1935, **3**, 1, 650.

[57] *Proc. Roy. Soc.*, 1935, [*A*], **150**, 576; *A.*, 1194; *Nature*, 1935, **135**, 268; cf. (Sir) W. H. Bragg, *ibid.*, 1934, **134**, 138; *A.*, 1934, 948.

[58] *Trans. Faraday Soc.*, 1934, **30**, 801.

[59] R. G. Wood, S. H. Ayliffe, and N. M. Cullinane, *Phil. Mag.*, 1935, [vii], **19**, 405; E. Hertel and E. Dumont, *Z. physikal. Chem.*, 1935, [*B*], **29**, 112; E. Hertel, *ibid.*, p. 117; F. Würstlin, *Z. Krist.*, 1934, **88**, 185; *A.*, 1934, 1162; B. Gossner and H. Neff, *ibid.*, **89**, 417; *A.*, 1935, 152; J. Dhar and A. C. Guha, *ibid.*, 1935, **91**, 123; M. Prasad and P. H. Dalal, *Current Sci.*, 1934, **3**, 200; *A.*, 1935, 152; K. Banerjee and B. C. Guha, *Indian J. Physics*, 1934, **9**, 287.

[60] *Chem. and Ind.*, 1935, **54**, 732; *Z. Krist.*, 1935, **91**, 450; *A.*, 1195.

Carbohydrates.—The structure of the sugars is one of the most difficult problems to be attacked by the methods of *X*-ray crystallography. The shapes of the molecules depart very far from the simple plane and linear varieties which have been dealt with already with such success, and little or no help can be got from optical data to assist any intensive simple crystal analysis. *X*-Ray data of a preliminary character have, however, continued to accumulate, both of simple mono-, di-, and tri-saccharides and their methyl, acetyl, and other derivatives,[62] and E. G. Cox, T. H. Goodwin, and (Miss) A. I. Wagstaff [63] have recently undertaken the review of the results obtained from some sixty substances. The hardness, high melting point, and high densities of the crystals suggest that the crystal structure of the sugars is largely determined by the hydroxyl groups, which tend to interact to the greatest possible extent and link the molecules together in all directions in the lattice. Any alteration in the groups attached to the ring, therefore, usually requires a complete readjustment of the relative positions of the hydroxyl groups and hence of the molecules themselves. There is consequently very little relation at first sight between the dimensions of unit cells of different compounds obtained by *X*-ray data. In the methylated sugars, however, the interactions between molecules are greatly reduced, and here Cox has found it possible to correlate directly the *X*-ray data with the shape and orientation of the molecule.

The shape of the molecule must depend on the stereochemical configuration of the pyranose ring on which it is based, and about this there has been considerable doubt. The most probable alternatives appear to be those drawn in Fig. 12, either one of the Sachse forms (*cis* and *trans*) found in *cyclo*hexane derivatives or the flat ring, previously discussed by Cox with reference to α-methylglucoside. In this ' flat ' ring the carbon atoms are probably in one plane, the oxygen slightly lifted out of it. In the Sachse rings it is possible for hydroxyl groups to be so attached that they lie either directly in the ring or approximately at right angles to it, and this should lead to markedly different values for the thickness to be observed for the molecules in the two cases. In the ' flat ' ring no such distinction exists.

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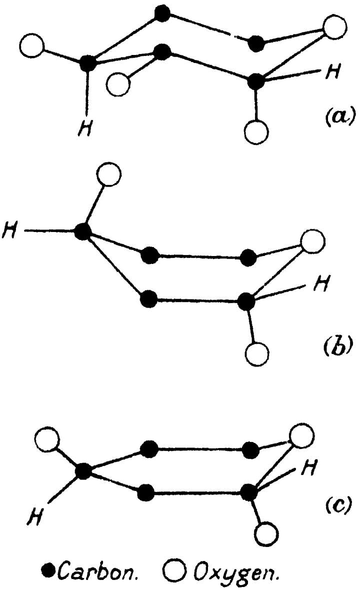
[61] J. M. Robertson, R. P. Linstead, and C. E. Dent, *Nature*, 1935, **135**, 506; J. M. Robertson, *J.*, 1935, 615.

[62] H. Braekken, C. J. Koren, and N. A. Sörensen, *Z. Krist.*, 1934, **88**, 205; *A.*, 1934, 1162; G. Vavrinecz, *Magyar Chem. Fol.*, 1933, **39**, 40; *A.*, 1934, 18; G. L. Leuck and H. Mark, *J. Amer. Chem. Soc.*, 1934, **56**, 1959; *A.*, 1934, 1162; K. Hess and K. Dziengel, *Ber.*, 1935, **68**, [*B*], 1594; *A.*, 1226; C. Trogus and K. Hess, *ibid.*, p. 1605; *A.*, 1308; S. B. Hendricks, *Nature*, 1934, **133**, 178; *A.*, 1934, 241.

[63] *J.*, 1935, 978, 1495; *A.*, 1195.

FIG. 12.

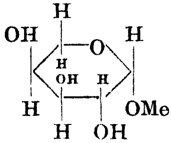


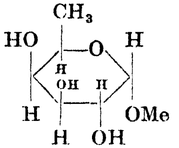
Possible configuration of the pyranose ring.

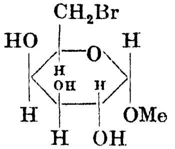
Cox finds that the crystal structure of the methylated sugars provides a means for distinguishing the two cases. These tend to form long needles with an identity period along the needle axis in many cases of only about 4·5 Å.—too short a distance to refer to anything but the molecular thickness. Cox has collected 26 examples of sugars in which one unit cell dimension is of this order of magnitude, since such measurements give unequivocally a value for the maximum size of the thickness. His results show that there is very little difference between the thicknesses measured for sugars having different configurations of the methoxyl groups.

For example, the maximum 'thickness' found for α-lactose, 4·69 Å., is very little greater than that of the three β-methylglucosides, 4·41—4·45 Å., and that of hexamethyl lyxosido-lyxoside is even smaller, 4·20 Å. This therefore suggests that the ring structure present is of the 'flat' variety.

Cox also finds certain very interesting examples of morphotropic relations between the crystal forms of related substances. The unit cell dimension of β-methylarabinoside, α-methylfucoside, and α-methylgalactoside 6-bromohydrin are given in the table.







	β-Methylarabinoside.	α-Methylfucoside.	α-Methylgalactoside 6-bromohydrin.
d_{100}	8·10	9·96	10·58
b	7·74	7·87	7·81
c	5·89	5·72	2×5·62

These inter-relations bear out the correctness of the configurations assigned on chemical and optical properties to these three compounds, and also incidentally indicate the presence of the pyranose ring in α-methylfucoside.

An exact knowledge of the configuration of the pyranose ring should prove an important aid towards the complete solution of the structure of cellulose, the problem of which has recently been reopened by M. Mathieu.[64] There is now a considerable accumulation of data on the reactions of cellulose and various derivatives.[65] *X*-Ray measurements have also been made on chitin by K. H. Meyer and G. W. Pankow,[66] who find an arrangement of chitobiose units in the unit cell closely related to cellulose. Starch micelles have been shown to be surrounded by a layer of water which is actually crystalline [67] and an attempt has also been made to follow the various changes that occur in micellar structure during breadmaking.[68] Other interesting observations are those on the molecular structure of sisal, coir, and oak,[69] and on pine tracheids.[70] The photographs of coir, for example, show two patterns of cellulose chains crossed at 45° to one another, and in pine tracheids a single spiral of cellulose is formed.

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[64] *Compt. rend.*, 1934, **198**, 1434; *A.*, 1934, 587; *Chim. et Ind.*, 1934, **31**, Spec. No. 792; *A.*, 1934, 760; see also W. A. Sisson, *Textile Res.*, 1935, **5**, 119; *A.*, 1308; G. Champetier, *Bull. Soc. chim.*, 1934, [v], **1**, 613; *A.*, 1934, 993; J. Barsha and H. Hibbert, *Canadian J. Res.*, 1934, **10**, 170; *A.*, 1934, 515.

[65] C. Trogus and K. Hess, *Cellulosechem.*, 1934, **15**, 1; *A.*, 1934, 244; *Ber.*, 1935, **68**, 1986; K. Hess, C. Trogus, and G. Abel, *Cellulosechem.*, 1935, **16**, 79; *A.*, 1356; K. Hess, C. Trogus, W. Eveking, E. Garthe, and N. Ljubitsch, *Annalen*, 1933, **506**, 260, 295; **507**, 62; *A.*, 1933, 1280; K. Hess and M. Ulmann, *Ber.*, 1934, **67**, [*B*], 2131; *A.*, 1935, 201; J. J. Trillat, *J. Chim. physique*, 1934, **31**, 125; *A.*, 1934, 479; M. Mathieu, *Compt. rend.*, 1934, **199**, 55; *A.*, 1934, 956; C. Trogus and K. Hess, *Z. Elektrochem.*, 1934, **40**, 193; T. Tomonari, *ibid.*, p. 207; *A.*, 1934, 637; M. Wadano, K. Hess, and C. Trogus, *Z. physikal Chem.*, 1935, [*B*], **30**, 159, 170, 183; J. J. Trillat, *J. Phys. Radium*, 1934, [vii], **5**, 207; *A.*, 1934, 834.

[66] *Helv. Chim. Acta*, 1935, **18**, 589; *A.*, 753.

The Structure of the Proteins.—Since, on present chemical theory, the proteins are built of amino-acids united by peptide links, one obvious method of approaching the problem of their structure is to study the simpler synthetic polypeptides. K. H. Meyer and Y. Go [71] have now made *X*-ray measurements of di-, tri-, tetra-, penta-, hexa-, and hepta-glycylglycine, and also of a polyglycylglycine of molecular weight about 2000 obtained from glycocoll carbonate. Unfortunately, only powder photographs could be obtained, but these show decreasing crystallinity in passing along the series, the photograph of heptaglycylglycine being very similar to those of the polyglycylglycine. From the tetrapeptide onwards the strongest spacings seem to be at 4·15 Å. and 3·15 Å., with the former finally dominating. This suggests a relatively simple arrangement of the chains in layers 4·2 Å. apart.

These photographs do not bear any very marked resemblance to those which have been obtained from natural fibres such as fibroin and keratin.[72] But this could hardly be expected, since in the natural fibres the hydrogen of glycine is substituted by a number of different groups—the R groups of the general formula. This produces an anisotropy in the directions perpendicular to the fibre axis, which should be shown in the method of packing the chains in the fibres. It is with this theoretical possibility that Astbury associates the two spacings observed in a great number of sclero-proteins of 4·65 Å. and 10—11 Å. The first, the backbone spacing, is very constant in a large number of proteins. The second, the side-chain spacing, varies somewhat from one species to another, as would be expected with the varying nature of the R groups. Photographs taken of the fibres in the usual way about the fibre axis show both spacings on the equatorial layer, and it is not possible to determine their mutual orientation. Astbury has, however, discovered that orientation of the keratin crystallites can be effected by lateral pressure in the presence of steam or hot water.[73] The keratin molecule is first transformed from the α-(contracted) to the β-(expanded) form by the pressure, and the crystallites then turn so as to bring the 'side-chain' spacing normal to the plane of flattening. The backbone spacing proves to be very accurately at right angles to this. The observations provide strong confirmation for Astbury's picture of the β-keratin structure as one of extended polypeptide chains, the most marked periodicity along the chain being one of 3—4 Å.

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[67] N. H. Kolkmeijer and J. C. L. Favejee, *Z. Krist.*, 1934, **88**, 226; *A.*, 1934, 1162.

[68] J. R. Katz and A. Weidinger, *Z. physikal. Chem.*, 1934, **169**, 321, 339; **171**, 181; *A.*, 1934, 1070; 1935, 165.

[69] E. N. Miles Thomas and J. Hewitt, *Nature*, 1935, **136**, 69; W. T. Astbury, R. D. Preston, and A. G. Norman, *ibid.*, p. 391; J. Hewitt, *ibid.*, p. 647.

[70] R. D. Preston, *Phil. Trans.*, 1935, [*B*], **224**, 131.

[71] *Helv. Chim. Acta*, 1934, **17**, 1488; *A.*, 1935, 152.

[72] W. T. Astbury, *Kolloid-Z.*, 1934, **69**, 340; *A.*, 1935, 162; F. Halle, *ibid.*, p. 324; *A.*, 1935, 162; W. T. Astbury and H. J. Woods, *Phil. Trans.*, 1933, [*A*], **232**, 333; *A.*, 1934, 352.

All the interconversion phenomena found between α- and β-keratin, including the transformation by pressure described above, have now been observed also with myosin, the protein of muscle.[74] Thus, myosin forms fibres which, on being roughly stretched parallel, show an *X*-ray photograph resembling that of α-keratin. On further stretching, the β-keratin photograph appears, which may be 'set' by exposure to steam, but the fibres, like those of keratin, are elastic and, provided the fibre has not been stretched and dried, will contract again. Other studies have been made on actual tissues,[75] and the α → β-transformation, in particular, has been observed in frog's sartorius muscle and the retractor muscle of the foot of *Mytelus edulis.*[75a]

So far the polypeptide theory of protein structure very adequately accounts for the simpler *X*-ray diffraction effects obtained from the scleroprotein fibres and films. It is more difficult at first sight to relate such a structure to the properties of the soluble proteins. These behave in the ultracentrifuge as if built up of large, approximately spherical molecules of molecular weight 35,000 or some multiple of this, and the presence of molecules of this order of magnitude has now been proved also by the *X*-ray diffraction effects obtained from crystalline pepsin and insulin. The early attempts to obtain diffraction effects for crystalline proteins failed to show more than two diffuse amorphous rings at about 10 and 4·3 Å.—

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[73] W. T. Astbury and W. A. Sisson, *Proc. Roy. Soc.*, 1935, [*A*], **150**, 533; *A.*, 1195.

[74] W. T. Astbury and S. Dickinson, *Nature*, 1935, **135**, 95; *A.*, 376.

[75] E. Saupe, *Kolloid-Z.*, 1934, **69**, 357; *A.*, 1935, 231; A. Küntzel and F. Prakke, *Biochem. Z.*, 1933, **267**, 243; *A.*, 1934, 316; F. Worschitz, *Fortschr. Röntgenstrahlen*, 1934, **50**, 174; *A.*, 1935, 1003; (with J. von Herman), *ibid.*, p. 178; *A.*, 1935, 1021; H. Kolpak, *Naturwiss.*, 1934, **22**,, 72; *A.*, 1934, 244.

[75a] W. T. Astbury and S. Dickinson, *Nature*, 1935, **135**, 765; *A.*, 772.

Astbury's side-chain and back-bone spacings respectively. These, from their appearance, had to be attributed to an amorphous rather than to a truly crystalline structure. The detection of the latter was made possible by J. D. Bernal's observation [76] that most protein crystals readily lose water on exposure to the air, so that the crystals as usually examined were only pseudomorphs. By taking photographs of crystals of pepsin immersed in the mother-liquor, he was able to obtain a true crystalline diffraction pattern, and this procedure has since been followed for a number of other proteins, *e.g.*, haemoglobin, edestin, and excelsin.[77] Imperfect powder photographs of urease and pepsin had previously been obtained by I. Fankuchen.[78] With insulin it has been found that the crystals remain unchanged on drying, so that here no precautions are required to obtain crystalline diffraction effects.[79]

Only in the case of pepsin and insulin are the data yet sufficient to give some information as to the size and shape of the units present, and these structures appear to be related to one another in a rather interesting way. In both cases, approximately spheroidal molecules of molecular weight about 37,000 appear to be present, but the packing is very different. In insulin the unit cell is rhombohedral, with $a = 44{\cdot}3$, $\alpha = 115°$, and contains a single Svedberg unit of weight 37,000. The size and shape of this molecule therefore follow as equivalent to the size and shape of the unit cell, and the packing together of the molecules is determined exactly by the lattice present. It is actually of a very close 8-co-ordination type. Pepsin, on the other hand, has a rhombohedral cell of dimensions $a = 162$ Å., $\alpha = 23°50'$, with a cell molecular weight 1,464,000. As this contains about 50% of water, only six Svedberg molecules of molecular weight about 37,000 are present in the cell. It is impossible in this case to say exactly how these molecules are arranged or what is their shape; but comparison of the cell dimensions and intensities of pepsin with insulin suggests strongly that the pepsin molecules are approximately spherical with radius 20 Å. and arranged in a loose 4-co-ordination structure probably related to that of β-carborundum. Such a structure leaves large channels between the pepsin molecules to be filled with water or with the many impurities from which it is extremely difficult to free the protein completely.

So far this work gives us no information as to what is the actual arrangement of the amino-acid residues inside these globular protein molecules, or what is their relation to the fibre proteins, but evidence of the connexion between the two is coming from several directions. Amongst the fibre proteins, on the one hand, very long spacings have been observed for feather keratin by W. T. Astbury and T. C. Marwick,[80] for tendon by Wyckoff, Corey, and J. Biscoe,[81] and for a number of materials such as collagen, gelatin, and nerves (though these latter are more probably due to lipins) by G. L. Clark and his co-workers.[82] These long spacings point either to the presence of large molecules or to the regular repetition at large intervals along the chain of some particular pattern of amino-acid residues. Such a pattern might be produced by the breakdown of some special configuration of atoms on the denaturation of a soluble protein. Astbury has accordingly studied this process in a number of the plant globulins, and finds that denaturation does in all cases lead to considerable sharpening of the very diffuse rings observed at 4·5 and 10 Å.[83] Moreover, denatured fibres of edestin (from crystals of which Wyckoff has reported typical long spacings) have all the elastic properties of the fibre proteins and give a well-oriented fibre pattern showing the typical spacings 3·3 Å. along the fibre axis and 10 and 4·5 Å. across it.[84] Still more illuminating results have been obtained on single crystals of excelsin, a plant globulin of molecular weight 200,000. By keeping this in water, Astbury was able to obtain a single-crystal pattern showing very large spacings, but superimposed on this was a typical fibre pattern which proved to be definitely oriented with respect to the crystal axes. After the exposure, the crystal was no longer soluble, although in shape and appearance it remained unaltered. An insoluble fibrous protein had evidently been obtained by some process of degeneration within the crystal. This suggests strongly that, whatever the configuration of the amino-acid residues is within the molecule, it is one that can be converted with very little change of the mutual positions of the atoms into a fibre form. But whether we should imagine the soluble protein as built up of scleroprotein chains, or the scleroproteins as having some other structure related in an unknown way to a new and different configuration of residues in the soluble proteins, remains still to be proved. D. M. C.

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[76] *Nature*, 1934, **133**, 794; *A.*, 1934, 720; cf. W. T. Astbury and R. Lomax, *bid.*, p. 795; *A.*, 1934, 720.

[77] R. W. G. Wyckoff and R. B. Corey, *Science*, 1935, **81**, 365.

[78] *J. Amer. Chem. Soc.*, 1934, **56**, 2398.

[79] (Miss) D. M. Crowfoot, *Nature*, 1935, **135**, 591.

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[80] *Nature*, 1932, **130**, 309. [81] *Science*, 1935, **82**, 175; *A.*, 1266.

[82] G. L. Clark, E. A. Parker, J. A. Schaad, and W. J. Warren, *J. Amer. Chem. Soc.*, 1935, **57**, 1509; *A.*, 1195; F. O. Schmitt, G. L. Clark, and J. N. Mrgudich, *Science*, 1934, **80**, 567; *A.*, 1935, 231; F. O. Schmitt, R. S. Bear, and G. L. Clark, *ibid.*, 1935, **82**, 44; *A.*, 1145.

[83] W. T. Astbury and R. Lomax, *J.*, 1935, 846.

[84] W. T. Astbury, S. Dickinson, and K. Bailey, *Biochem. J.*, 1935, **29**, 2351; *A.*, 1433.

LIQUIDS.

It is impossible for reasons of space to include in this section all the modern developments in the theory of liquids. All that can be done is to give some references to recent papers on the determination of the statistical structure of certain liquids by means of *X*-rays.

S. Katzoff [85] has studied water, heptane, decane, benzene, and *cyclo*hexane: in water, a tetrahedral arrangement was found;[86] in the others, a statistical close packing of chains or quasispherical molecules. B. E. Warren [87] has made a Fourier analysis of liquid paraffin and shows that it can be represented by parallel zigzag chains at an average distance of 5·0 Å. apart.

W. H. Zachariasen [88] has shown that in liquid methyl alcohol there is evidence for hydroxyl bonds. J. A. Prins has studied the diffraction of ionic solutions,[89] and been able to show that a secondary lattice depending on the concentration exists in some, but not all, ionic solutions.

The question of cybotactic groups has been much studied, especially by Stewart and his co-workers.[90] Evidence is still conflicting. These groups almost certainly do exist in long-chain alcohols, but their presence in ethyl ether in the region of the critical point has been disputed by N. S. Gingrich and B. E. Warren,[91] who show that the observed diffraction can be explained simply by a statistical arrangement of a certain mean distance. It is interesting to note that the diffraction pattern given by liquids in the neighbourhood of the critical point depends only on the volume, and is practically identical at two temperatures above and below the critical temperature when these have the same volume.

H. Sirk [92] has shown, by unsuccessful attempts to induce magnetic orientation, that the cybotactic group in a hydrocarbon cannot contain more than 10,000 molecules. J. D. B.

J. D. BERNAL.
D. M. CROWFOOT.
R. C. EVANS.
A. F. WELLS.

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[85] *J. Chem. Physics*, 1934, **2**, 841; *A.*, 1935, 152. Compare H. K. Ward, *ibid.*, p. 153; *A.*, 1934, 587; W. C. Pierce, *ibid.*, 1935, **3**, 252; J. A. Prins and R. Fonteyne, *Physica*, 1935, **2**, 573.

[86] See *Ann. Reports*, 1934, **31**, 86.

[87] *Physical Rev.*, 1933, [ii], **44**, 969; *A.*, 1934, 244.

[88] *J. Chem. Physics*, 1935, **3**, 158.

[89] *Ibid.*, p. 72; J. A. Prins and R. Fonteyne, *Physica*, 1935, **2**, 570; J. A. Prins, *ibid.*, 1934, **1**, 1171; *A.*, 1935, 162.

[90] G. W. Stewart, *J. Chem. Physics*, 1934, **2**, 147; *A.*, 1934, 591; C. A. Benz and G. W. Stewart, *Physical Rev.*, 1934, [ii], **46**, 703; R. D. Spangler, *ibid.*, p. 698; *ibid.*, 1932, [ii], **42**, 907; *A.*, 1933, 1236.

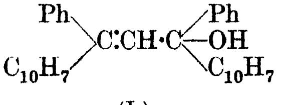
[91] *Ibid.*, 1934, [ii], **46**, 248; *A.*, 1934, 1160.

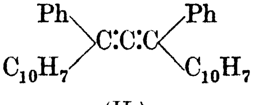
[92] *Z. Physik*, 1934, **89**, 129; *A.*, 1934, 834.

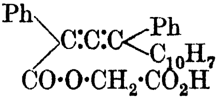
ORGANIC CHEMISTRY.

1. STEREOCHEMISTRY.

ONE of the ambitions of all stereochemists has been realised by P. Maitland and W. H. Mills,[1] who have shown that an allene can exhibit the optical activity required of it by established theory. They dehydrated $\alpha\gamma$-diphenyl-$\alpha\gamma$-di-1-naphthylallyl alcohol (I) with *d*- and with *l*-camphor-10-sulphonic acid and obtained *d*- and *l*-diphenyldinaphthylallene (II), the specific rotations (λ 5461) having the surprisingly high values + 437° and − 438°.

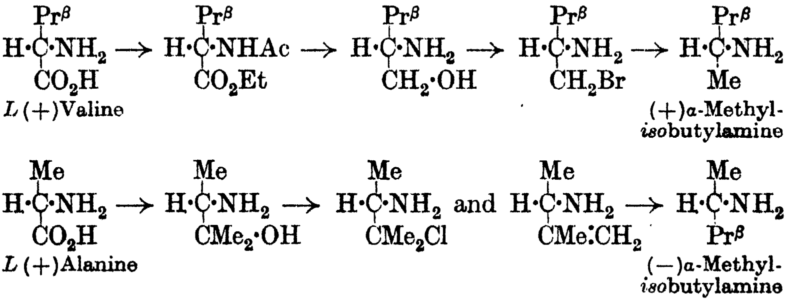

(I.)


(II.)


(III.)

Part of the credit for the resolution of an allene is also due to E. P. Kohler, J. T. Walker, and M. Tishler,[2] who have isolated, from the brucine salts, carboxymethyl $\alpha\gamma$-diphenyl-γ-naphthylallene-α-carboxylate (III) in enantiomeric forms, with $[\alpha]_D$ + 29·5° and − 28·4°. Further developments of both of these researches will be awaited with more than usual interest.

F. Barrow and G. W. Ferguson,[3] by carrying out the two series of changes,



$$\underset{CO_2H}{\overset{Pr^{\beta}}{H\cdot C\cdot NH_2}} \rightarrow \underset{CO_2Et}{\overset{Pr^{\beta}}{H\cdot C\cdot NHAc}} \rightarrow \underset{CH_2\cdot OH}{\overset{Pr^{\beta}}{H\cdot C\cdot NH_2}} \rightarrow \underset{CH_2Br}{\overset{Pr^{\beta}}{H\cdot C\cdot NH_2}} \rightarrow \underset{Me}{\overset{Pr^{\beta}}{H\cdot C\cdot NH_2}}$$

L(+)Valine (+)α-Methyl-*iso*butylamine

$$\underset{CO_2H}{\overset{Me}{H\cdot C\cdot NH_2}} \rightarrow \underset{CMe_2\cdot OH}{\overset{Me}{H\cdot C\cdot NH_2}} \rightarrow \underset{CMe_2Cl}{\overset{Me}{H\cdot C\cdot NH_2}} \text{ and } \underset{CMe{:}CH_2}{\overset{Me}{H\cdot C\cdot NH_2}} \rightarrow \underset{Pr^{\beta}}{\overset{Me}{H\cdot C\cdot NH_2}}$$

L(+)Alanine (−)α-Methyl-*iso*butylamine

show that naturally occurring dextrorotatory valine, called *L*(+) valine, has the same configuration as (+)alanine.

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[1] *Nature*, 1935, **135**, 994; *A*., 968.

[2] *J. Amer. Chem. Soc.*, 1935, **57**, 1743; *A*., 1363.

[3] *J*., 1935, 410; *A*., 736.

K. Freudenberg and M. Meister[4] have confirmed their previous view that *l*-lactic acid has the same configuration as natural *d*-alanine.

Additional evidence[5] which goes to prove that ethyl (—)β-hydroxy-β-phenylpropionate, $Ph{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2Et$, has the same configuration as ethyl (—)β-chloro-β-phenylpropionate, $Ph{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2Et$, is afforded by the reactions of the *p*-toluenesulphinic and the *p*-toluenesulphonic ester of the former compound. The (+)sulphinate reacts with chlorine and with hypochlorous acid to give, respectively, the (—)chloro-ester and the (—)hydroxy-ester. Since these reactions are of a similar type, it follows that the (—)chloro-ester and the (—)hydroxy-ester arise with inversion and have like configurations. The (+)sulphonate reacts with acetic acid and with lithium chloride to give, respectively, the (—)acetoxy-ester, $Ph{\cdot}CH(OAc){\cdot}CH_2{\cdot}CO_2Et$, and the (—)chloro-ester. Since the (+)acetoxy-ester is produced by the action of acetic anhydride on the (+)hydroxy-ester, it follows that these two reactions of the (+)sulphonate are accompanied by inversion, and therefore that the (—)chloro-ester and the (—)hydroxy-ester have like configurations.

From an examination[6] of a considerable number of reactions of the *p*-toluenesulphonates of *d*-β-butanol, *d*-β-octanol, and *d*-benzylmethylcarbinol, it would appear that these esters react with salts, Grignard reagents, pyridine, and phenol with inversion of configuration. With ammonia and piperidine, the *d*-β-butyl and the *d*-β-octyl *p*-toluenesulphonate may react without inversion, but the results suggest that *d*-benzylmethylcarbinyl *p*-toluenesulphonate reacts with ammonia and piperidine with inversion.

An interesting example of activation has been observed by A. McKenzie and E. W. Christie,[7] who have produced activation of racemic acid by adding *d* (or *l*)-malic acid to solutions of potassium racemate. The necessary solubility controls were made.

From time to time, total asymmetric syntheses have been recorded. T. L. Davis and R. Heggie[8] caused bromine to combine with 2 : 4 : 6-trinitrostilbene in presence of right circularly polarised light. The stated changes in observed angle during three different experiments were: 0·000°, 0·036°, 0·013°; 0·000°, 0·040°, 0·000°; 0·000°, 0·029°, 0·009°. By comparison with work of a similar kind, this result must be counted as a positive one.

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[4] *Annalen*, 1935, **518**, 86; *A.*, 849.

[5] J. Kenyon, H. Phillips, and G. R. Shutt, *J.*, 1935, 1663.

[6] J. Kenyon, H. Phillips, and (Miss) V. P. Pittman, *ibid.*, p. 1072; *A.*, 1230.

[7] *Biochem. Z.*, 1935, **277**, 122; *A.*, 731.

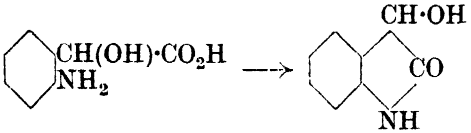
[8] *J. Amer. Chem. Soc.*, 1935, **57**, 377; *A.*, 480.

The effect of complex salt formation on the rate of racemisation of optically active α-phenylethyl chloride has been studied by K. Bodendorf and H. Böhme.[9] The formation of a complex salt with a metallic chloride, MCl,

$$\mathrm{CHPhMeCl} + \mathrm{MCl} \rightleftharpoons \mathrm{CHPhMe[MCl_2]} \rightleftharpoons \mathrm{CHPhMe^+} + \mathrm{[MCl_2]^-},$$

would be expected to accelerate racemisation owing to the production of free $\mathrm{CHPhMe^+}$ ions. A purely catalytic effect on the part of MCl is possible,[10] however, and it is found that hydrogen chloride, lithium chloride, and tetramethylammonium chloride do accelerate racemisation slightly, and in fact to the same degree. On the other hand, mercuric chloride, which is little ionised by comparison with these chlorides, is approximately fifty times as effective as a catalyst as they are. Zinc chloride also catalyses the racemisation of the phenylethyl chloride, and its effect is destroyed by lithium chloride, in proportion to the amount of the latter present, owing to the preferential formation of $\mathrm{Li[ZnCl_3]}$. The effectiveness of mercuric chloride depends on the dielectric properties of the medium : it is, for example, much greater in nitrobenzene that in acetone, and greater still in ether. Yet stannic chloride is much more effective in benzene than it is in nitrobenzene. Boron trichloride is more active than mercuric or zinc chloride, but arsenious and silicon chlorides are usually inactive. Antimony trichloride has very little catalytic effect, but that of antimony pentachloride is too great to permit of accurate measurement.

A. McKenzie and P. A. Stewart [11] have resolved *o*-nitromandelic acid. The active forms had the unusually high specific rotation, $[\alpha]_{5461}^{20^\circ} \pm 594^\circ$, in acetone solution. Reduction of the lævo-form with ferrous sulphate and baryta led to the corresponding (—) amino-acid, which, in presence of mineral acid, passed into (+)dioxindole :



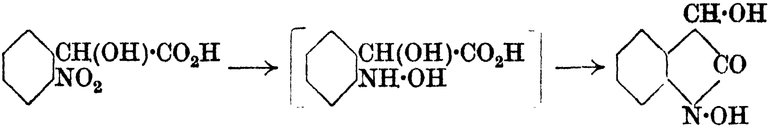
Similarly, the (+)amino-acid gave rise to a (—)dioxindole, and the pure dioxindoles were obtained with $[\alpha]_{5461}^{20^\circ} \pm 40^\circ$, in acetone. Reduction of the (+)nitromandelic acid with zinc dust and am-

[9] *Annalen*, 1935, **516**, 1; *A.*, 454.

[10] R. Kuhn and T. Wagner-Jauregg, *Naturwiss.*, 1929, **17**, 103; *A.*, 1929, 425; T. Wagner-Jauregg, *Monatsh.*, 1929, **53—54**, 791; *A.*, 1929, 1423.

[11] *J.*, 1935, 104; *A.*, 356.

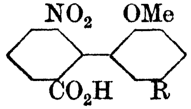
monium hydroxide, on the other hand, gave (—)*N*-hydroxydioxindole :

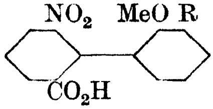


and again the cyclic reduction product was obtained as the two optically pure forms, with $[\alpha]_{5461}^{20^\circ}$ ± 59°, in acetone.

R. Adams and his collaborators have continued their investigation of diphenyl and related compounds. Some time ago [12] it was shown that variation of R (in the 5′-position) in the acid (IV) produced definite variation in the rate of racemisation. In a more recent paper [13] the effect of the same substituents when in the 3′-position (V) is described. The results, shown below, clearly demonstrate that substitution in the 3′-position has far more effect than substitution in the 5′-position :

(IV.)





(V.)

Half-life periods (minutes) in EtOH at about 25°.

R	H	OMe	Me	Cl	Br	NO$_2$
Half-life period (IV)	9·4	10·8	11·5	31·0	32·0	35·4
,, ,, (V)	9·4	98·1	331·9	711·3	827·0	1905·2

The authors conclude that the weight of R is not a factor in slowing down semicircular oscillations, since chlorine and bromine have almost the same effect, which is less than that of nitroxyl. They think the greater effect produced in the 3′-position is possibly due to a repulsion effect, since the more polar the substituent R the larger is the effect. There can be little doubt that the valency directions of methoxyl and R in the 3′-series will be "splayed," but other effects are conceivable, which the authors may have considered but do not appear to have mentioned. The effective size of the methoxyl group must be less or greater if the oxygen atom is respectively more positive or more negative than it is in the parent acid. The above results show, however, that the nitro-acids in both series are the most stable, although here the oxygen atoms in the methoxyl groups are presumably most positive owing to the pull on their electrons by the nitro-group. It is therefore possible that the determining factor may be the rigidity of the

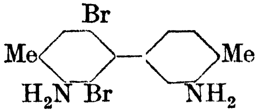
[12] H. C. Yuan and R. Adams, *J. Amer. Chem. Soc.*, 1932, **54**, 4434; *A.*, 1933, 63.

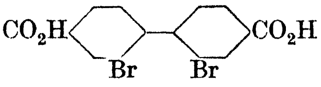
[13] S. L. Chien and R. Adams, *ibid.*, 1934, **56**, 1787; *A.*, 1934, 1101.

methoxyl–nucleus bond, which affects the ease with which the group is turned aside, and would be greatest when the oxygen atom is pulled most strongly towards the nucleus (effect of nitro-group large). Clearly, however, this would explain only part of the facts.

Another striking result [14] obtained in the same laboratories is the partial resolution of 2 : 6-dibromo-3 : 3′-diamino-4 : 4′-ditolyl (VI). The actual angle observed for the *d*-base was only + 0·18°, but in addition the camphorsulphonate was shown to undergo mutarotation in solution. Although the quantitative results need amplifying, it appears that the active base is less easily racemised than an active 2 : 2′-dibromodiphenyl-4 : 4′-dicarboxylic acid (VII).[15] The effectiveness of the 2-bromine atom in (VI) must be considerably increased by the presence of the amino-group in the 3-position. In contrast to this, it is important to note the reported fairly ready racemisation [16] of 4 : 6 : 4′ : 6′-tetrabromodiphenic acid (VIII), since this acid would be expected to have quite high optical stability.

(VI.)

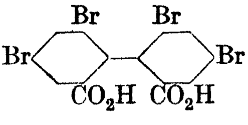




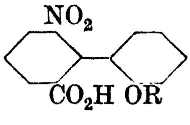
(VII.)

C. C. Li and R. Adams [17] have determined the velocities of racemisation and the heats of activation for the three acids (IX), where R = Me, Et, or Pr^a. The heats of activation were about the same in all three cases (about 20,000 cals.), yet the approximate order of ease of racemisation in six different solvents was OMe>OEt>OPr^a, the propyl ether being approximately seven times as stable as the methyl ether. This result is not unexpected, but is a very useful contribution, particularly in connexion with the rotational effects of obstacle groups.

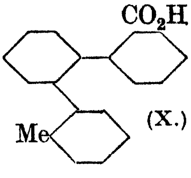
A. M. Sadler and G. Powell [18] explain their failure to resolve the acid (X) as being due to "synchronised rotation" of the nuclei, but in view of the difficulty of resolutions in the diphenyl series this conclusion will not be generally accepted.



(VIII.)



(IX.)



(X.)

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[14] W. I. Patterson and R. Adams, *J. Amer. Chem. Soc.*, 1935, **57**, 762; *A.*, 742.

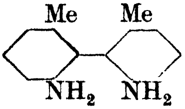
[15] N. E. Searle and R. Adams, *ibid.*, 1934, **56**, 2112; *A.*, 1934, 1351.

[16] H. C. Yuan and T. T. Hsü, *J. Chinese Chem. Soc.*, 1935, **3**, 206; *A.*, 1237.

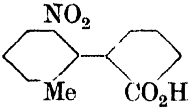
[17] *J. Amer. Chem. Soc.*, 1935, **57**, 1565; *A.*, 1364.

[18] *Ibid.*, 1934, **56**, 2650; *A.*, 1935, 211.

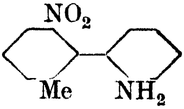
F. Bell[19] has obtained further evidence that obstacle groups can undergo displacement reactions without racemisation ensuing. Optically active 2 : 2′-diamino-6 : 6′-dimethyldiphenyl (XI) was converted into the corresponding 2 : 2′-di-iodo- and the 2 : 2′-difluoro-compound, both of which were optically active. Similarly, conversion of (XII) into (XIII) by either the Hofmann or the Curtius reaction did not cause complete loss of optical activity.



(XI.)

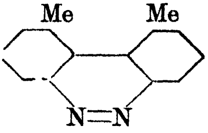


(XII.)

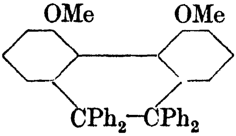


(XIII.)

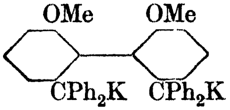
G. Wittig and D. Stichnoth[20] have prepared the phenazone (XIV). It formed a well-defined *d*-α-bromocamphor-π-sulphonate, but this could not be resolved. The result recalls the inactivity[21] of the dihydrophenanthridine (XV) when this substance was produced from the optically active potassium derivative (XVI) of the related dibenzhydryldiphenyl.



(XIV.)



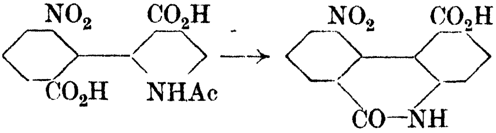
(XV.)



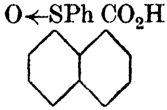
(XVI.)

Similarly, S. Sako,[22] who has effected the complete resolution of 6-nitro-6′-acetamidodiphenic acid (XVII), finds that the active acid is converted into inactive 5-nitrophenanthridone-4-carboxylic acid (XVIII) when heated with sulphuric acid. If (XVIII) is really planar, it is clear that there is very little room for the nitroxyl and the carboxyl group, and it would not be surprising if the *l*-menthyl ester (say) of the acid proved to be a mixture of diastereoisomerides.

H. G. Rule and H. McN. Turner[23] have described the partial



(XVII.) (XVIII.)



(XIX.)

[19] *J.*, 1934, 835; *A.*, 1934, 884.

[20] *Ber.*, 1935, **68**, [*B*], 928; *A.*, 858.

[21] G. Wittig and H. Petri, *Annalen*, 1933, **505**, 27; *A.*, 1933, 944.

[22] *Bull. Chem. Soc. Japan*, 1934, **9**, 393; *A.*, 1934, 1351.

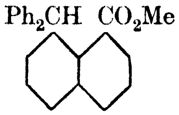
[23] *J.*, 1935, 319; *A.*, 618.

optical resolution of phenyl 8-carboxy-1-naphthyl sulphoxide (XIX). Mutarotation in acetone solution was not observed and it appears to be concluded that it is impossible to predict the practical interference effect in such cases.

An interesting example of steric hindrance is described by G. Wittig and H. Petri,[24] who find that methyl 8-benzhydryl-1-naphthoate (XX) is unaffected by phenylmagnesium bromide, but is readily converted into the corresponding carbinol ($CO_2Me \longrightarrow CPh_2{\cdot}OH$) by phenyl-lithium.

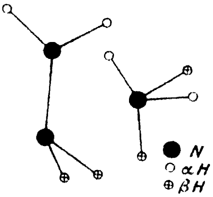
(Miss) M. S. Lesslie and E. E. Turner[25] have effected the complete resolution of 10-ethylphenoxarsine-2-carboxylic acid, which presumably has a folded structure. The same authors[26] failed to resolve 2 : 10-dimethyl- or 10-phenyl-2-methyl-phenoxarsine metho-*d*-camphor-10-sulphonate or -*d*-α-bromocamphor-π-sulphonate, as was to be expected.

It has always seemed probable to the writer that if ever optical activity is shown to be associated with the presence of an " asymmetric nitrogen atom," it is most likely to be discovered among the hydrazines, and it is interesting to find[27] that from dipole measurements hydrazine itself has the configuration shown by (XXI) (elevation) and (XXII) (plan).



(XX.)

(XXI.)



(XXII.)

Similar work with nuclear-substituted phenylhydrazines by H. Ulich, H. Peisker, and L. F. Audrieth[28] confirms the above view, and it is pointed out that certain disubstituted hydrazines should exhibit stereoisomerism, and that even with monosubstituted hydrazines two crystalline modifications may be possible.

Considerable interest attaches to the first[29] of a series of papers on leucoanthocyanins and leucoanthocyanidins. By extracting sawdust of the heartwoods of *Peltogyne porphyrocardia* (" purple heart "), the authors have succeeded in isolating a leucoanthocyanidin, peltogynol, which is optically active. Hot nitric acid converts it into styphnic acid, and oxidation of its *O*-trimethyl ether gives 4 : 5-dinitroveratrole or *m*-hemipinic acid according to the conditions. These facts, in conjunction with the results of an *X*-ray crystallographic examination by Miss D. M. Crowfoot, suggest that peltogynol is (XXIII).

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[24] *Ber.*, 1935, **68**, [*B*], 924; *A.*, 858.

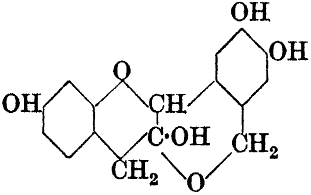
[25] *J.*, 1935, 1268; *A.*, 1390.

[26] *Ibid.*, p. 1051; *A.*, 1257.

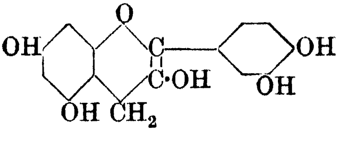
[27] W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, 1934, **30**, 898; *J. Chem. Physics*, 1934, **2**, 492; *A.*, 1934, 1158.

[28] *Ber.*, 1935, **68**, [*B*], 1677; *A.*, 1304.

[29] (Mrs.) G. M. Robinson and R. Robinson, *J.*, 1935, 744; *A.*, 985.

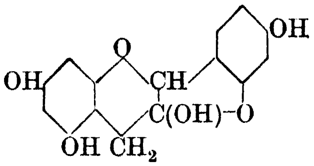


(XXIII.)



(XXIV.)

(XXV.)



Cyanomaclurin, regarded by A. G. Perkin[30] as probably being (XXIV), is shown[31] to be best represented by (XXV). It is optically active, and appears to be optically stable.

E. E. T.

2. POLYMERISATION.

The processes of polymerisation have attracted a good deal of attention during recent years owing to the industrial importance of high-molecular materials. The term *polymerisation* is now used by many authors to include processes of aggregation by condensation, as well as those of orthodox type, and various examples of "condensation-polymerisation" are described below.

Mechanism of Chain Growth.

Hypothesis of Stepwise Addition.—In former Reports[1] reference has been made to suggestions that polymerides are built up by the addition of monomeric molecules at the double bond of monomeric, dimeric, trimeric, etc., units in succession, each addition being of the type $\cdot\mathrm{C{:}C}\cdot + \mathrm{HX} \longrightarrow \cdot\mathrm{CH{\cdot}CX}\cdot$. The successive additions of the monomeric units involve (*in effect* at any rate) the separation of hydrogen as one of the components of the addendum molecule, and the scheme as a whole is frequently referred to as the *hydrogen-separation hypothesis*.

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[30] *J.*, 1905, **87**, 715.

[31] H. Appel and R. Robinson, *J.*, 1935, 752; *A.*, 985.

[1] *Ann. Reports*, 1930, **27**, 91; 1931, **28**, 87; 1932, **29**, 11.

This mechanism of reaction is held to apply to the formation not only of dimerides such as those of *iso*butene, *as*-diphenylethylene, α-methylstyrene, and indene, but also of trimerides, etc., and of at least certain high polymerides, such as those of indene. This scheme, when applied to high polymerides, is opposed to the *macropolymerisation hypothesis* of H. Staudinger.[2]

It is clear, however, that if hydrogen separation (actual, incipient, or potential) is postulated as a necessary feature of polymeric reaction, a monosubstituted olefin, $\mathrm{R{\cdot}CH{:}CH_2}$, might in the general case be expected to give four dimerides, although usually only one or two would be likely to arise in significant quantity :

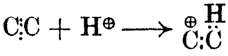
$$\begin{array}{l}
\mathrm{R{\cdot}CH{:}CH_2 + H{\cdot}CR{:}CH_2 \longrightarrow CH_3{\cdot}CHR{\cdot}CR{:}CH_2} \\
\mathrm{R{\cdot}CH{:}CH_2 + H{\cdot}CR{:}CH_2 \longrightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}CR{:}CH_2} \\
\mathrm{R{\cdot}CH{:}CH_2 + H{\cdot}CH{:}CHR \longrightarrow CH_3{\cdot}CHR{\cdot}CH{:}CHR} \\
\mathrm{R{\cdot}CH{:}CH_2 + H{\cdot}CH{:}CHR \longrightarrow R{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CHR}
\end{array}$$

Actually, two dimerides, differing only in the position of the double bond, have been obtained from *iso*butene :[3] one of these may be derived from the other by secondary change, or both may arise as a consequence of the normal mechanism controlling dimerisation. The number and character of the dimerides arising by mild polymerisation of propene and Δ^1-butene do not seem to have been determined (see, however, p. 255).

At the trimeric stage the structure of the polymerides of even simple olefins becomes difficult to determine experimentally. It has been ascertained, however, in one case, *viz.*, that of *iso*butene : here the tri*iso*butene derived by the action of sulphuric acid on the monomeric substance or on *iso*butyl alcohol contains the substances (I)—(IV).[4]

$$\begin{array}{llll}
\text{(I.)} & \mathrm{CMe_3{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CMe_3} & \mathrm{(CMe_3{\cdot}CH_2)_2C{:}CH_2} & \text{(II.)} \\
\text{(III.)} & \mathrm{CH_2{:}CMe{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe_3} & \mathrm{CMe_2{:}CH{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe_3} & \text{(IV.)}
\end{array}$$

F. C. Whitmore[4a] regards the polymerisation in this case as being promoted by acid catalysis, the first step being the addition of a hydrogen ion to the extra pair of electrons in the double bond :



$$\mathrm{C}\vdots\mathrm{C} + \mathrm{H}^{\oplus} \longrightarrow \overset{\oplus\,\mathrm{H}}{\mathrm{C}{:}\ddot{\mathrm{C}}}$$

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[2] *Ann. Reports*, 1929, **26**, 105.

[3] R. J. McCubbin and H. Adkins, *J. Amer. Chem. Soc.*, 1930, **52**, 2547; *A.*, 1930, 1017.

[4] R. J. McCubbin, *ibid.*, 1931, **53**, 356; *A.*, 1931, 333.

[4a] *Ind. Eng. Chem.*, 1934, **26**, 94; see also J. B. Conant and G. W. Wheland, *J. Amer. Chem. Soc.*, 1933, **55**, 2499; *A.*, 1933, 804.

Then the positively charged carbon atom of the product can undergo the changes characteristic of an atom with a deficiency of electrons.* According to this mechanism the reaction mixture would contain at the dimeric stage the two olefins $CH_2{:}CMe{\cdot}CH_2{\cdot}CMe_3$ and $CMe_2{:}CH{\cdot}CMe_3$, which are actually found to be the components of di*iso*butene, and also *iso*butene and two positive groups (*tert.*-butyl and *iso*octyl). If the mechanism is followed out to the trimeric stage, the formation of the four dodecenes (I—IV) can easily be formulated.

The scheme is capable of application to the tetra*iso*butenes, the constitutions of which have not yet been determined experimentally, and to higher polymerides. It is especially to be noted that any olefin present in the reaction mixture constitutes a potential addendum, but the possibilities are complicated (a) by the possible reversal of additions of positive groups to olefins, and (b) by rearrangement of the positive groups formed by addition to olefins.

If the hypothesis of hydrogen separation is accepted, the separation from the addendum (actually or by mere polarisation) of positive components other than the proton may be envisaged. In the dimerisation of amylene brought about by the action of sulphuric acid on *iso*propylcarbinol G. M. Kline and N. L. Drake [5] regard the amylene molecule, $CMe_2{:}CHMe$, as more prone to activation by polarisation in the manner $\overset{\ominus}{C}H_3{-}\overset{\oplus}{C}Me{:}CHMe$ † than by incipient separation of $H^{\oplus}$; they do not, however, preclude the latter. On this assumption the two actually observed diamylenes (V) and (VI) can be formulated as arising from the two hydrocarbons which normally result from the dehydration of the carbinol, thus :

$$CMe_2{:}CHMe + CH_3{-}CMe{:}CHMe \longrightarrow CH_3{\cdot}CMe_2{\cdot}CHMe{\cdot}CMe{:}CHMe \quad (V.)$$

$$CEtMe{:}CH_2 + CH_3{-}CMe{:}CHMe \longrightarrow CEtMe_2{\cdot}CH_2{\cdot}CMe{:}CHMe \quad (VI.)$$

The formation of isomeric di*iso*butenes and tri*iso*butenes can be similarly formulated, although, in representing the formation of the various trimeric substances, a capacity for incipient separation of both $Me^{\oplus}$ and $H^{\oplus}$ is assumed, and the polarised addendum is in some cases a monomeric molecule (*i.e.*, monomeride added to dimeride) and in others a dimeric molecule (*i.e.*, dimeride added to monomeride). It is readily seen that on these lines the number of theoretically possible isomerides for pentamerides, hexamerides, etc., would be extremely great.

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[5] *J. Res. Nat. Bur. Stand.*, 1934, **13**, 705; *A.*, 1935, 192.

* These include : (1) union with a negative ion, X, having a complete octet of electrons, simple addition of HX to the double bond thus being completed; (2) reversal of the process by loss of the same or a different proton to give the same or a new olefin; (3) rearrangement of the carbon skeleton, followed by loss of a proton, to give a new olefin; and (4) polymerisation (*i.e.*, the addition of the positive organic fragment to another molecule of olefin in the same way that the proton was added to the first molecule of olefin), the resulting larger positive fragment being itself capable of undergoing the changes (1)—(4).

If in change (4) the larger positive fragment undergoes polymerisation, it may either add to an olefin molecule, or lose a proton to give an olefin molecule to which a positive fragment may add. The process is envisaged as continuing in this way until large sluggish molecules are obtained.

† The incipient separation of methyl rather than of hydrogen is justified by the authors on the ground of the greater strength of the C–H bond than of the C–C bond.

G. S. Whitby holds that the stepwise-additive mechanism applies not only to the formation of low polymerides, but also to polymerides of moderate molecular weight (polyindenes)[6] and of high molecular weight (polystyrenes);[7] in consequence, the individual polymerides in the different series all contain of necessity one double bond per molecule. The view is based experimentally on the bromine-absorbing capacity of the polymerides, and the fact that the dipole moments of polyindenes and polystyrenes increase with increase of molecular size.[8] Indene can be added to di-indene, on heating, to give tri-indene, and styrene if heated with distyrene appears definitely to participate in the (additive) production of lower (about 13-molecular) polystyrenes; furthermore, several of the lower polyindenes are known to be themselves polymerisable under the action of heat or of catalysts. Evidence contributed by R. C. Houtz and H. Adkins shows that the molecules of polystyrenes in a polymeric product can be "lengthened" by re-treatment of the latter (after its first isolation) with monomeric styrene in presence of a catalyst.[9] All these facts are consistent with the view that a succession of stepwise additions is involved in the formation of long chains by polymerisation.

Macropolymerisation and Chain-reaction Mechanism.—According to Staudinger's hypothesis of macropolymerisation[2] the polymerisation of styrene, indene, allyl chloride, formaldehyde, etc., may be considered to proceed by the "opening" of the double bonds of the monomeric molecules, followed by head-to-tail linking of the forms so activated.* The free terminal valencies were at first supposed to be ineffective as centres of unsaturation owing to the large size of the molecule;[10] later the idea of tervalent carbon at

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[6] *J. Amer. Chem. Soc.*, 1928, **50**, 1160; *A.*, 1928, 627; *Canadian J. Res.*, 1931, **4**, 344; *A.*, 1931, 833.

[7] *Trans. Faraday Soc.*, 1936, **32**, 315.

[8] W. Gallay, *Kolloid-Z.*, 1931, **57**, 1; *A.*, 1931, 1231.

[9] *J. Amer. Chem. Soc.*, 1933, **55**, 1609; *A.*, 1933, 600.

[10] H. Staudinger, *Ber.*, 1920, **53**, 1082; *A.*, 1920, i, 517; H. Staudinger and J. Fritschi, *Helv. Chim. Acta*, 1922, **5**, 787; *A.*, 1922, i, 1043.

* More recently formulated as a chain mechanism :

$$\cdot CHR\cdot CH_2\cdot + nCHR{:}CH_2 \longrightarrow \cdot CHR\cdot CH_2\cdot[CHR\cdot CH_2]_{n-1}\cdot CHR\cdot CH_2\cdot$$

the ends of the long-chain molecules was replaced by the assumptions of cyclisation and of the acquisition of " foreign " end groups,[11] although the experimental recognition of the latter in long-chain hydrocarbons does not appear to have been very successful; recently H. Staudinger and A. Steinhofer seem inclined to consider that the polymeric chains with free end-valencies acquire terminal double bonds by intermolecular migration of hydrogen.[12]

From a consideration of the velocities of reaction in polymerisations which appear undoubtedly to proceed by stepwise additions, W. Chalmers [13] has calculated, on the assumption that the rates of the consecutive reactions are not greater than the rate of dimerisation, that the chief polymerides produced will be the lower ones, and that the proportion of these will rapidly fall off with increasing complexity so that less than 0·5% will exceed decameric magnitude. In true macropolymerisations the experimental results do not conform with this conclusion: indeed, styrene, vinyl acetate, the acrylic esters, etc., give polymeric mixtures the complexity of which is so much greater than the limit fixed by the stepwise theory that this can no longer be entertained. A few polymerisations, such as those of olefins by sulphuric acid, are considered to take place by an abbreviated series of stepwise reactions and these are regarded as confirming the above deduction, since, besides a predominant quantity of dimeride and trimeride, only inconsiderable amounts of tetrameride and higher polymerides are formed. Indeed the small proportions of the earlier members in the various polymeric products from styrene, vinyl acetate, etc., show that the velocity of addition of monomeride to the existing dimeride, trimeride, etc., must be much greater than that of the primary coupling of monomeric molecules. This absence of appreciable proportions of the lower polymerides has been observed at the beginning of, and during, the polymerisation in the cases that have been investigated.[14] Chalmers considers that the polymerisation proceeds as a chain reaction.

The first stage in the chain-reaction mechanism is the formation of "nuclei," *i.e.*, activated molecules or reactive radicals. The activation required at this stage can be thermal, photochemical, or catalytic.[15]

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[11] H. Staudinger, A. A. Ashdown, M. Brunner, H. A. Bruson, and S. Wehrli, *Helv. Chim. Acta*, 1929, **12**, 934; *A.*, 1929, 1435; H. Staudinger, " Die hochmolekularen organischen Verbindungen," Berlin, 1932, p. 213.

[12] *Annalen*, 1935, **517**, 35; *A.*, 611.

[13] *J. Amer. Chem. Soc.*, 1934, **56**, 917; *A.*, 1934, 607.

[14] H. Staudinger and H. W. Kohlschütter, *Ber.*, 1931, **64**, [*B*], 2091; *A.*, 1931, 1270; H. Staudinger, *Trans. Faraday Soc.*, 1936, **32**, 104.

[15] M. Dostal and H. Mark, *ibid.*, p. 54; C. E. H. Bawn, *ibid.*, p. 182; see also E. K. Rideal, *ibid.*, p. 5.

In the thermal polymerisation of olefins such as styrene, the collision of two monomeric molecules with sufficiently high energy may be assumed to cause activation by " opening " the two double bonds and forming doubly unsaturated (activated) radicals, $\cdot CHX\cdot CH_2\cdot CHX\cdot CH_2\cdot$.

When photochemical polymerisation (*e.g.*, of butadiene, acrylic esters) is in question, the monomeric molecule is activated by absorption of light and becomes able to form a nucleus when colliding with an ordinary non-active molecule. In catalytically promoted polymerisations (*e.g.*, that of butadiene by sodium or of chlorobutadiene by oxygen) the catalyst appears to increase the velocity of formation of polymerisation nuclei by " adsorption " on the double bond.

The nucleus may then collide with a monomeric molecule of the initial substance, combine with it, and grow in this way. This and the subsequent reactions doubtless have a low activation energy, and the velocity of chain-growth can therefore be high, compared with the velocity of formation of nuclei. The chain is thus built up by successive additions of monomeric molecules to the rapidly growing activated molecule;* it may be terminated by collision with a foreign molecule or by inhibition of activity due to the large size of the molecule.†

Course of Polymeric Reaction.

Olefins.—Although there seems little doubt that the low polymerides of olefins and also many of the higher ones are ordinarily mono-olefinic, yet the information as to the course of polymeric reaction as it is determined (a) by the molecular constitution of the monomeric substance, and (b) by the experimental conditions, is meagre. Experiments on the polymerisation of propene at 125° in the presence of phosphoric acid [16] indicate that the hydrocarbon forms esters with the catalyst : these esters readily decompose at the temperature of polymerisation, yielding activated olefin molecules which unite to form polymerides. The first-formed hexene may react with phosphoric acid to form hexylphosphoric acid, which in turn may react with propylphosphoric acid to form nonylene. In an analogous way either nonylphosphoric acid in reaction with propylphosphoric acid, or two molecules of hexylphosphoric acid, may yield dodecene :

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[16] V. N. Ipatieff, *Ind. Eng. Chem.*, 1935, **27**, 1067.

* Presumably the chain pattern is not in all cases necessarily strictly regular (*i.e.*, *all* the component units arranged head to tail), especially where the growth of the chain has been interrupted, *e.g.*, by isolation of the polymeride, and afterwards continued. The skeletal pattern of G. S. Whitby's polymerisation products starting from di-indene, distyrene, and tristyrene would be of interest.

† For alternative routes of reaction, see M. Dostal and H. Mark (ref. 15).

$$C_3H_6 \longrightarrow C_6H_{12} \longrightarrow C_9H_{18} \longrightarrow C_{12}H_{24}$$

In the polymerisation of mixtures of olefins, *e.g.*, propene-butene, there appear not only the respective polymerides of each hydrocarbon, but also mixed polymerides.* It is suggested that the formation of these may be represented thus :

$$C_3H_7{\cdot}O{\cdot}PO(OH)_2 + C_4H_9{\cdot}O{\cdot}PO(OH)_2 \longrightarrow C_7H_{14} + 2PO(OH)_3$$

F. C. Whitmore[17] finds, in confirmation of the work of F. H. Gayer,[18] that olefins differing in composition from the expected multiples of C_3-molecules are formed from propene at 350° : in this case pentene (mainly $CMe_2{:}CHMe$) and octene (containing $CMe_2{:}CMePr$) appear to be formed. In the dipropene fraction, $CMe_2{:}CHEt$, $CMe_2{:}CMe_2$, and a *saturated* hydrocarbon, CMe_2Pr, occur, and in the C_7-fraction a mixture of *heptanes* is found.

The tendency of aluminium chloride to yield cyclic products with olefins, even at low temperatures, has previously been recognised. Experiments by H. I. Waterman and J. J. Leendertse at 0° to −80° show that the fraction of molecular weight 350 obtained by its aid from Δ^{β}-pentene definitely contains one ring per molecule, and the branched-chain pentenes give fractions which are partly cyclic. At higher temperatures the proportion of cyclic material increases.[19]

Conjugated Dienes. Low Polymerides.—When conjugated dienes are polymerised, whether spontaneously or by thermal or catalytic means, they yield in general two types of polymeride, *viz.*, (1) oily cyclic dimerides † and (2) rubber-like polymerides which are heterogeneous in molecular size and probably not invariably uniform in their skeletal pattern. The cyclic dimerides are not further polymerisable to caoutchoucs and are not intermediates in the passage of dienes into caoutchoucs; moreover, their formation has not, so far as is known, any special significance in relation to the mechanism of the high-polymerisation process by which caoutchoucs are formed. Polymerisation, then, amongst conjugated dienes can proceed by at least two routes. A few trimeric polymerides of open-chain dienes (doubtless partly cyclic) have been obtained, *viz.*, a trimeride of isoprene,[20] also a trimeride and apparently a tetrameride from βγ-dimethylbutadiene.[21]

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[17] *Trans. Faraday Soc.*, 1936, **32**, 232.

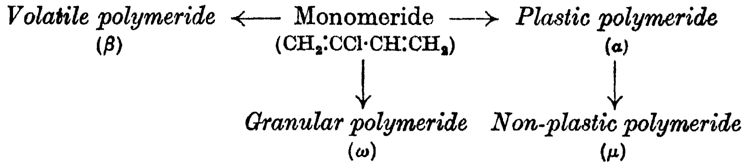
[18] *Ind. Eng. Chem.*, 1933, **25**, 1122; *B.*, 1933, 997.

[19] *Rec. trav. chim.*, 1935, **54**, 79; *A.*, 192; *Trans. Faraday Soc.*, 1936, **32**, 251.

* Compare the reported union of dimeric and trimeric *iso*butene under the action of heat (Lebedev and Kobliansky, *Ber.*, 1930, **63**, [*B*], 103, 1432; *A.*, 1930, 316, 1017).

† These are substituted *cyclo*hexenes containing two double bonds, but one apparent exception to the rule has been reported (E. Bergmann, *J.*, 1935, 1359; *A.*, 1497). No artificially formed open-chain dimerides of dienes are known, but two such dimeric structures occur naturally, *viz.*, ocimene and myrcene, related to isoprene.

High Polymerides (*Rubbers*).—The characteristics, and the conditions determining the formation, of polychloroprenes (see scheme below) have now been more fully described.[22, 23]



The terpene-like β-polymeride is an undesirable by-product in rubber synthesis, but its formation becomes appreciable only at temperatures higher than that necessary to promote rapid formation of α-polyprene. The plastic α-polymeride (corresponding to unvulcanised rubber) is formed at moderate temperatures and passes rapidly into the ω-polymeride (corresponding to vulcanised rubber), especially at higher temperatures. The ω-polymeride, useless as an artificial rubber, often appears during very slow polymerisation and its formation is favoured by strong ultra-violet light and metal surfaces: it is made up of discrete rubber particles, non-plastic and unswelled by rubber solvents. When a speck of ω-polymeride appears or is introduced into a specimen of incompletely polymerised chloroprene, the entire specimen is soon more or less completely converted into ω-polymeride: its growth apparently occurs at different rates in different directions and its structural character is probably closely analogous to cauliflower-like masses which appear spontaneously by polymerisation of liquid isoprene, butadiene, and dimethylbutadiene.

J. R. Katz, however, has found that the *X*-ray patterns of the cauliflower-like polymerides resemble those of the corresponding polymerisates formed from the liquid dienes by the action of (a) heat and (b) sodium in presence of carbon dioxide, but they differ from those of the polymerisates formed by the action of sodium alone.[24] Since the low-boiling butadienes have the same amorphous pattern as the thermal high-polymerides made from them —a point which agrees with the Staudinger conception of the constitution of the latter $(\cdot\underset{1}{C}\cdot\underset{2}{C}{:}\underset{3}{C}\cdot\underset{4}{C}\cdot\underset{1}{C}\cdot\underset{2}{C}{:}\underset{3}{C}\cdot\underset{4}{C}\cdot)$—it would seem that only the sodium polymerisate has an abnormal carbon skeleton.* Polychloroprene appears from its *X*-ray pattern to be a *trans*-form, like gutta-percha, and not a *cis*-form like rubber : it is therefore a derivative of gutta-percha rather than of rubber.

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[20] T. Wagner-Jauregg, *Annalen*, 1932, **496**, 52; *A.*, 1932, 856.

[21] R. G. Bacon and E. H. Farmer, unpublished work.

[22] W. H. Carothers, J. E. Kirby, and A. M. Collins, *J. Amer. Chem. Soc.*, 1933, **55**, 789; *A.*, 1933, 371.

[23] W. H. Carothers, *Trans. Faraday Soc.*, 1936, **32**, 42.

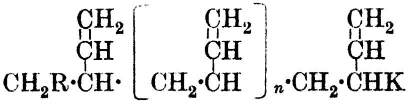
[24] J. R. Katz, J. Selman, and Lottelise Heyne, *Kautschuk*, 1927, 214; J. R. Katz, *Trans. Faraday Soc.*, 1936, **32**, 83.

K. Ziegler has examined the mechanism of butadiene polymerisation in the presence of sodium, lithium, and metallic alkyls.[25] His data for the action of sodium on the hydrocarbon (and these are borne out by an examination of the kinetics of the reaction by A. Abkin and S. Medvedev [26]) point to the following general mechanism. Butadiene first reacts with sodium, developing primary additive disodio-compounds (reaction A); the reaction of polymerisation then consists in the successive additions of butadiene molecules to these compounds (reaction B).

$$\mathrm{CH_2{:}CH\cdot CH{:}CH_2 + 2Na \longrightarrow Na\cdot CH_2\cdot CH{:}CH\cdot CH_2Na} \quad \text{(A)}$$

$$\mathrm{Na\cdot CH_2\cdot CH{:}CH\cdot CH_2Na + 2CH_2{:}CH\cdot CH{:}CH_2 \longrightarrow ({:}CH\cdot CH_2\cdot CH_2\cdot CH{:}CH\cdot CH_2Na)_2} \quad \text{(B)}$$

If the butadiene reacts with the sodio-organic compound at its 1 : 4-carbon atoms, the polymerisation process can be viewed as a successive inclusion of butadiene molecules between the carbon and the sodium of the sodio-organic compound, thus bringing the sodium continuously to the surface of the polymeride where it can react with adsorbed butadiene; but since the kinetic results do not point to a surface reaction, it seems probable that the linking of butadiene molecules occurs largely at the 1 : 2-positions. The process resembles formally a chain reaction, but here the active centres (sodio-butadiene compounds) are transitory products of reaction and their rate of formation is significantly less rapid than the subsequent addition of butadiene to the sodio-organic compounds. The polymerising action of potassium alkyls, RK, is similar, the polymeride, if 1 : 2-attachments be assumed, being representable as in (C). The polymerides obtained by metals



$$\mathrm{CH_2R\cdot\overset{\overset{\overset{\overset{CH_2}{\|}}{CH}}{|}}{CH}\cdot\left[CH_2\cdot\overset{\overset{\overset{\overset{CH_2}{\|}}{CH}}{|}}{CH}\right]_n\cdot CH_2\cdot\overset{\overset{\overset{\overset{CH_2}{\|}}{CH}}{|}}{CHK}}$$

(C)

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[25] K. Ziegler and K. Bähr, *Ber.*, 1928, **61**, 253; *A.*, 1928, 404; K. Ziegler, F. Crossmann, H. Kleiner, and O. Schäfer, *Annalen*, 1929, **473**, 1; *A.*, 1929, 1091; K. Ziegler and H. Kleiner, *ibid.*, p. 57; *A.*, 1929, 1091; K. Ziegler, F. Dersch, and H. Wollthan, *ibid.*, 1934, **511**, 13; *A.*, 1934, 864; K. Ziegler, L. Jakob, H. Wollthan, and A. Wentz, *ibid.*, p. 64; *A.*, 1934, 865.

[26] *Trans. Faraday Soc.*, 1936, **32**, 286.

* K. Harries (1912) found that the ozonides of the sodium and the sodium–carbon dioxide polymerides decomposed into different substances.

and metallic alkyls have often comparatively low molecular weights (penta- to deca-meric).

Influence of Substituents on Polymerisation Capacity.—Numerous observations have been made on the very important influence of substituents in promoting or inhibiting the polymerisation of basic systems. Certain broad tendencies are referred to by H. Staudinger [27] and by G. S. Whitby.[28] No detailed correlation of substituent influences, however, appears to be possible at present.

Characteristics of High-polymerides.

High-polymerides are peculiar in that they alone among organic materials display to a significant degree such mechanical properties as strength, elasticity, and hardness; their practical uses depend almost entirely on these properties, which in turn depend on the size and shape of the macromolecules. The synthetic high-polymerides—and no distinction is here intended between true polymerides and the multi-condensation products described below—resemble in many of their properties the high-molecular substances of natural origin, and can be used as more or less adequate substitutes for them; also like natural high-molecular substances, they dissolve with strong swelling to form colloidal solutions and thus belong to the class of lyophilic colloids. As a class they possess considerable stability and have relatively simple structures; moreover, the results obtained with them are important in respect of the light they throw on the structure of such natural products * as caoutchouc [29] and cellulose.[30]

It is possible by variation of the conditions of preparation (temperature, catalyst, etc.) to form from the same initial substance (*e.g.*, styrene, vinyl acetate, or acrylic esters) polymerides with different chain lengths, but constructed according to the same principle. These substances, ranging in polymeric degree from 5,000- to 10,000-molecular (molecular weight 500,000 and upwards), differ only in chain length, and form polymeric homologous series;

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[27] *Trans. Faraday Soc,*, 1936, **32**, 286.

[28] G. S. Whitby and R. N. Crozier, *Canadian J. Res.*, 1932, **6**, 203; *A.*, 1932, 496; G. S. Whitby and W. Gallay, *ibid.*, p. 280; *A.*, 1932, 496.

[29] H. Staudinger, *Trans. Inst. Rubber Ind.*, 1935, **10**, No. 3.

[30] *Idem, Trans. Faraday Soc.*, 1933, **29**, 18; *A.*, 1933, 226; *Naturwiss.*, 1934, 797; *A.*, 1935, 70.

* Although many different types of synthetic polymerides (including multi-condensation products) have been manufactured, no naturally occurring polymerisation process has yet been exactly simulated. In the case of artificial rubber, for example, on the one hand only empirical methods of control have as yet been possible in conducting synthetic operations, and on the other hand it is doubtful whether the natural synthesis starts from a diene hydrocarbon as do the artificial ones.

and since the physical properties of high-polymerides change with the length of the macromolecules, it is possible to prepare from one and the same initial substance high-polymerides with very different physical properties. This fact is of great technical importance. H. Staudinger distinguishes between three main groups of molecular colloids, differing in the lengths of the thread-like molecules : [31]

(1) *Hemicolloids*, of molecular weight up to 10,000 (chain length, from 50 to 250 Å). These relatively short molecular threads have no very pronounced colloidal properties : they dissolve without swelling, forming solutions of low viscosity which obey the Hagen–Poiseuille law. The solids are powdery or glue-like masses ; filaments or films prepared from them have little tensile strength and are easily broken.

(2) *Mesocolloids*, of an order of polymerisation ranging from 100 up to about 1000 (chain length, 250—2,500 Å). These have properties intermediate between those of the hemicolloids and of the eucolloids.

(3) *Eucolloids*, of an order of polymerisation above 1000 (chain length, above 2,500 Å ; the longest thread molecules yet prepared are about 1μ long). These polymerides have the characteristic properties of lyophilic colloids : their dissolution is accompanied by intense swelling and their solutions are highly viscous, are abnormal even at low concentrations as regards flow phenomena, and do not obey Einstein's law. Eucolloidal substances show a high capacity for film formation and are often highly elastic ; the solid substances are very tough and hard. The technically most important substances belong to this group.

The classification holds for high-molecular substances of very diverse types so long as they are homopolar. The colloidal properties of heteropolar substances (*e.g.*, sodium polyacrylate) differ strongly from those of homopolar substances (*e.g.*, polyacrylic esters) even when both have the same chain length.

Three-dimensional Polymerisation.

Differences in Swelling Capacity of High-molecular Substances.—Certain lyophilic colloids, although of apparently identical composition, show great differences in their capacity for swelling and dissolution. Some swell to an unlimited extent, lose their form, and finally dissolve completely,* whereas others, apparently identical in composition with the first, swell in the same solvents up to a certain limit only. The latter colloids retain their form and remain undissolved even after long treatment with large quantities of the solvent, but their swelling capacity may nevertheless be very extensive, *e.g.*, the volume may increase to as much as 50—100 times its initial value.[32]

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[31] *Ber.*, 1929, **62**, [*B*], 2893; *A.*, 1930, 77; H. Staudinger and E. Husemann, *ibid.*, 1935, **68**, [*B*], 1691; *A.*, 1319.

* That is, dissolution occurs simultaneously with swelling.

Many natural products with a highly polymerised structure exist in two modifications, one of unlimited and the other of limited swelling capacity; *e.g.*, the α- and the β-form of caoutchouc [33] (the former being the ordinary soluble variety and the latter an insoluble variety of limited swelling capacity [34]), and corresponding soluble and insoluble forms of some proteins. No difference between the forms is revealed by chemical analysis, and the important differences in physical properties were at first regarded as " colloidal phenomena," for which an explanation was sought in the different micellar structures of the soluble and the insoluble modification rather than in their different molecular constitutions. The investigation of highly polymerised synthetic substances, however, has revealed that this view cannot be correct and Staudinger maintains that the variations in physical behaviour, even of colloids, are due to chemical differences in the molecular structure.[32] The macromolecules of the soluble colloid with their unlimited swelling capacity are different from those of the insoluble colloid of similar composition. The evidence is drawn largely from experiments with synthetic polystyrenes.

Mixed Polymerides.—When pure styrene is polymerised rapidly with the aid of catalysts (*e.g.*, stannic chloride), it gives hemicolloidal powders, soluble in organic solvents without swelling, and possessing a degree of polymerisation not exceeding 50—100. When, on the other hand, it is polymerised slowly at low temperatures, there are formed strongly swelling, eucolloidal products of an order of polymerisation not less than 1000—5000. The molecules of the latter, though longer than those of the simpler polymerides, are still thread-shaped.[35] If, now, styrene is adulterated with a little *p*-divinylbenzene and polymerisation is subsequently carried out at 60—100°, a " mixed " polymerised product of styrene and divinylbenzene is obtained. The mixed product resembles the eucolloidal product from pure styrene in forming a tough hard glass and is indistinguishable from it in chemical composition. Nevertheless, the "mixed" product differs from the "pure" polystyrene in being insoluble, although it is subject to a high degree of swelling in organic solvents.

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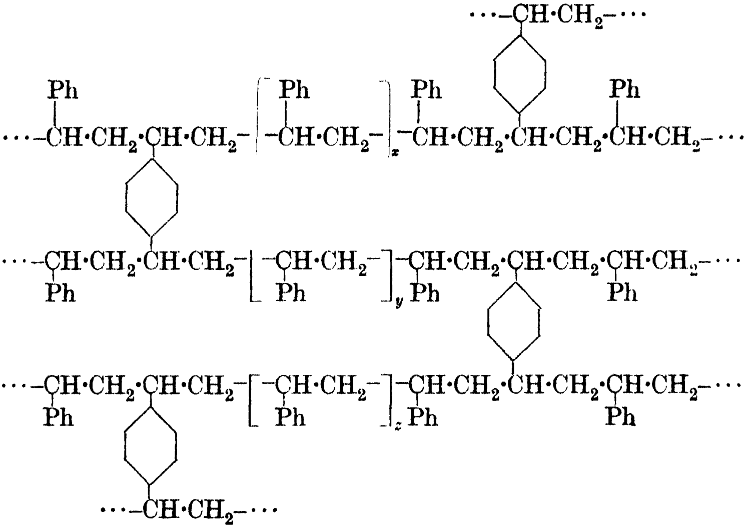
[32] H. Staudinger, W. Heuer, and E. Husemann, *Trans. Faraday Soc.*, 1936, **32**, 323.

[33] P. Bary and E. A. Hauser, *Z. Kautschuk*, 1928, 97.

[34] C. O. Weber and W. A. Caspari, *Ber.*, 1909, **33**, 779; W. A. Caspari, *J. Soc. Chem. Ind.*, 1913, **32**, 1041; H. Feuchter, *Kolloidchem. Beih.*, 1925, **20**, 434.

[35] H. Staudinger and W. Heuer, *Ber.*, 1934, **67**, [*B*], 1159; *A.*, 1934, 879.

Staudinger attributes the formation of insoluble products of restricted swelling capacity when divinylbenzene is used, to the establishment of divinylbenzene bridges linking the thread-molecules as shown in the formula :



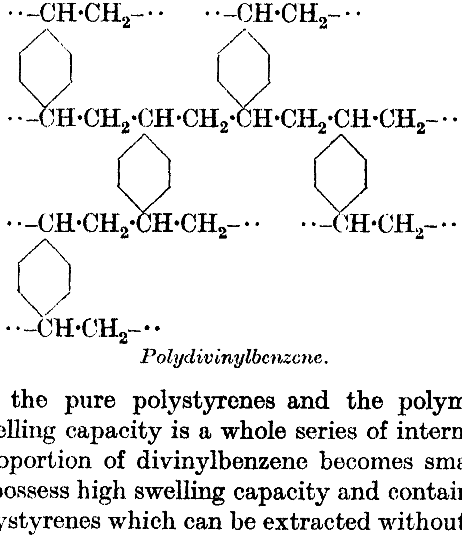
Mixed polymeride from styrene and divinylbenzene.

Here the "mixed" polymeride must be regarded as composed of macromolecules extending into *three dimensions*, and not of simple thread molecules, as was the case with "pure" polystyrene.

The quantity of divinylbenzene required to give the insoluble product in place of the soluble one is exceedingly small. One molecule of divinylbenzene per 10,000—50,000 molecules of monomeric styrene is sufficient (the precise amount depending on the conditions of polymerisation) and this corresponds to an addition of 0·01—0·002% of divinylbenzene—an amount not discoverable by ordinary chemical analysis.

The efficiency of the tiny amount of divinylbenzene in bringing about an important change in the physical properties of the polystyrenes is due to the fact that the soluble polystyrene is composed of very long chain-molecules; it is apparently sufficient to establish just a few links between adjoining macromolecules in order to make dissolution of the substance impossible. The swelling capacity remains, because the molecules retain their tendency to form solvates; but even after solvation they cannot leave the bulk of the substance, because they are linked together by the " bridges " formed by divinylbenzene.[35]

Staudinger has investigated the influence of the proportion of divinylbenzene used (and hence the number of links between the chains) on the swelling capacity of the product. The swelling capacity decreases with increase of the proportion of divinylbenzene, and at high concentrations of the latter there is hardly any swelling at all. Pure *p*-divinylbenzene, when polymerised at 60—100°, gives vitreous products, which, though resembling the eucolloidal polystyrenes, are wholly deficient in swelling capacity. The polydivinylbenzenes are very brittle and easily powdered: in this they are unlike the polystyrenes, which are mechanically stable; and the change in mechanical properties in passing from the one to the other is doubtless a reflexion of the concomitant structural change from thread-shaped to three-dimensional molecules. The constitution of the polydivinylbenzenes may be symbolised thus:[35]



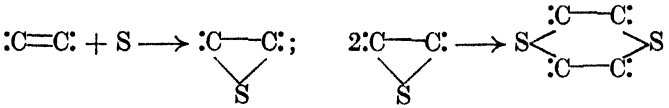
Polydivinylbenzene.

Connecting the pure polystyrenes and the polymeric products of limited swelling capacity is a whole series of intermediate forms. When the proportion of divinylbenzene becomes small, the mixed polymerides possess high swelling capacity and contain a proportion of soluble polystyrenes which can be extracted without changing the form of the remaining body; at still lower concentrations the divinylbenzene bridges become too weak to hold the substance together and the polymeride no more retains its form on swelling; ultimately, with further decrease in the concentration of divinylbenzene, the whole substance becomes soluble. But even after dissolution the polystyrene molecules remain linked in groups by divinylbenzene links: thus the average length of the dissolved molecules is greater than in solutions of pure polystyrenes, and the viscosity of the solutions is accordingly higher.

There is a connexion, but no direct proportionality, between the length of the polystyrene chains and the amount of divinylbenzene required for obtaining an insoluble product : longer (*e.g.*, eucolloidal) chains require a smaller proportion of divinylbenzene to yield an insoluble product than do shorter (*e.g.*, hemicolloidal) ones. It is doubtless true that in eucolloidal polymerides of limited swelling capacity not the whole of the polystyrene molecules are linked together by divinylbenzene bridges : these substances, therefore, must represent closely interwoven mixtures formed of three-dimensional macromolecules of the " mixed " polymeride and the thread-molecules of the pure polystyrene.

Soluble, Insoluble, and Vulcanised Caoutchouc.—Ordinary soluble (and intensely swelling) caoutchouc, when kept for a long time, becomes transformed into insoluble caoutchouc with limited swelling capacity. It can be made soluble again by mastication. It was therefore supposed that the transformation of the soluble into the insoluble form was a reversible process.[33] Subsequently the work of Staudinger showed that conversion of the soluble (α-) into the insoluble (β-) caoutchouc occurs only in presence of oxygen,[36] and the long-chain molecules of the α-form are apparently converted into three-dimensional molecules of the β-form by oxygen links between the chains. By masticating the insoluble caoutchouc, the three-dimensional molecules are broken up ; [35] at the same time the chains are shortened by oxidation. The " regenerated " soluble caoutchouc is therefore a highly degraded product ; the order of polymerisation of its molecules is not greater than 300—500, as against 1000—2000 of the original substance. Thus, according to Staudinger, the transformation of the soluble caoutchouc into the β-form is not a reversible colloidal process, but an irreversible change in the chemical structure of the macromolecules.

With regard to vulcanised rubber the bulk of evidence favours the view that vulcanisation is the result of cross-linking through reaction at the double bonds. According to W. H. Carothers the average rubber molecule contains probably at least 5000 double bonds : if, then, the reaction of rubber with sulphur is pictured as the passage *via* unstable sulphides into cross-linked molecules, as below,



at a minimum all the rubber molecules could be locked together when only 0·04% of the double bonds had disappeared, or when sulphur to the extent of about 0·02% of the weight of the rubber had reacted.[37] Experimentally the minimum amount of sulphur required for the beginning of vulcanisation is about 0·15%.[38]

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[36] H. Staudinger and H. F. Bondy, *Annalen*, 1931, **488**, 153; *A.*, 1931, 1067; H. Staudinger and E. O. Leupold, " Die hochmolekularen organischen Verbindungen, Kautzschuk und Cellulose," p. 443.

Multi-condensations (*Condensation-polymerisations*).

Owing mainly to the researches of W. H. Carothers, J. W. Hill, and their collaborators much information has been accumulated about these aggregations (so-called polymerisations) which in their nature are multi-condensations.* Molecules which contain two, three, or more groups capable of mutual interaction (*e.g.*, $\cdot OH$, $\cdot Cl$, $\cdot CO_2H$, NH_2) unite with elimination of simpler molecules (*e.g.*, H_2O, HCl, NH_3) to form chains of smaller or greater length, thus :

(I.) $CH_2(OH)_2 + CH_2(OH)_2 + nCH_2(OH)_2 \longrightarrow$

Formaldehyde (*hydrated*) $HO{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}[CH_2{\cdot}O]_{n-1}{\cdot}CH_2{\cdot}OH$

Polyoxymethylene

(II.) $nHO{\cdot}R{\cdot}CO_2H \longrightarrow HO{\cdot}R{\cdot}CO{\cdot}O{\cdot}R{\cdot}CO{\cdot}O{\cdot}[R{\cdot}CO{\cdot}O]_{n-2}{\cdot}H$

Polyester

(III.) $2HO_2C{\cdot}R{\cdot}CO_2H + nHO{\cdot}R'{\cdot}OH \longrightarrow$

$HO_2C{\cdot}R{\cdot}CO{\cdot}O{\cdot}R'{\cdot}O{\cdot}CO{\cdot}R{\cdot}CO{\cdot}[O{\cdot}R']_{n-1}{\cdot}OH$

Polyester

(R, R' = bivalent groups, *e.g.*, polymethylene)

Bi- and Multi-functional Reactions.—The reacting groups are termed *functions*, and the number of such groups in a molecule is referred to as the degree of functionality. The interacting molecules need not be of the same kind so long as all are at least of bifunctional degree, since it is clear that polyesterifications of the type represented in III belong to the same class of reactions as I and II.

In the formation of open-chain aggregates from bifunctional molecules, not all the functional groups react, since at least the end groups remain intact; but whereas at the dimeric or two-molecular stage in reactions such as I—III only half the groups have reacted, at higher stages the proportion of groups which have undergone reaction increases rapidly. Bifunctional reactions can yield only linear polymerides, and in the formation of such polymerides solubility and fusibility do not appear to be lost even at very high molecular weights. But reactions involving higher degrees of functionality always present the possibility of a spreading out into three dimensions, with formation of insoluble and infusible cross-linked molecules. If, for example, multi-condensed molecules, $\cdot AX_2\cdot AX_2\cdot AX_2\cdot AX_2\cdot$, containing two separate residual functions X in each *unit* of the chain,* were to interact, then obviously all the chains would become locked in a single molecule when (assuming that no intramolecular action occurs) only two functions per *chain-molecule* had been lost: this result would be achieved for chains 200 units long when only 1% of the residual functions had been lost, and would certainly be accompanied by the disappearance of fusibility and solubility.

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[37] W. H. Carothers, *Trans. Faraday Soc.*, 1936, **32**, 46.

[38] G. Bruni, *Rev. Gen. Caoutchouc*, 1931, **8**, No. 75; H. P. Stevens and W. H. Stevens, *J. Soc. Chem. Ind.*, 1932, **51**, 44T; *B.*, 1932, 33.

* Carothers regards *true* polymerisation, in which the combination of unsaturated molecules occurs additively without any elimination of smaller molecules, as only a special case of polymerisation. In this case the functional groups are the reactive ends of the double bonds.

If a fraction p of the total functional groups present in the reacting molecules undergoes reaction, then:

$$p \text{ (degree of reaction)} = 2/f - 2/xf$$

where f = the number of functional groups per monomeric (or original) molecule, and x = the average degree of polymerisation (dimeric, trimeric, hundred-molecular, etc.) as given by the ratio of the number of monomeric or original molecules initially present to the total number of molecules present after reaction has occurred.[39, 37] If in this formula x is very large, the second term disappears and we have $p = 2/f$, an expression that tells at what degree of reaction the molecular weight will become infinite.† When two different molecules of different degrees of functionality interact, the situation is more complicated, but the formula can often be usefully applied to determine the limits of intermolecular reaction.‡

Types of Polymeride.—During the last few years Carothers has extended his work on the interaction of dibasic acids and glycols (*i.e.*, polyesterification) [40] to include the formation of (1) linear

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[39] W. H. Carothers, *J. Amer. Chem. Soc.*, 1929, **51**, 2548; *A.*, 1929, 1165.

[40] *Ann. Reports*, 1930, **27**, 94.

* Multiple-function compounds often do not exercise all their functions at once.

† For example, the limiting value of p for a tetrafunctional reaction will be at ½; and since for the same reaction p = 49·5% at that point where x = 100, it follows that the average molecular weight can suddenly change from a moderate value to a colossal value with very little change in the degree of reaction; moreover, so far as the utility of the formula is concerned, it is unimportant whether the transition in properties occurs at a molecular weight of 10^5 or 10^{20}.

‡ Thus in the reaction of glycerol with phthalic anhydride (glyptal resins) the maximum amount of reaction under any distribution of combinations which can take place before gelation ($x = \infty$) sets in is 83·3% (compare G. Bozza, *Giorn. Chim. ind. appl.*, 1932, **14**, 400; *B.*, 1932, 1040), whereas the minimum degree of reaction compatible with gelation is 66·7%. Experimental values for the extent of reaction at gelation generally lie between 75% and 80% (G. Bozza, *loc. cit.*; R. H. Kienle and A. G. Hovey, *J. Amer. Chem. Soc.*, 1929, **51**, 509; *B.*, 1929, 293).

polymeric anhydrides of adipic,[41] sebacic,[42] and other acids,[43] and also Friedel–Crafts derivatives of these,[44] (2) linear polymeric amides from ε-aminohexoic acid,[45] (3) linear *super*polyesters from dibasic acids and glycols and also from ω-hydroxydecoic acid,[46] (4) linear *super*polyamides and mixed polyester-polyamides,[47] (5) linear *super*polyanhydrides,[42] (6) polyalcohols from decamethylene bis-(magnesium bromide),[48] (7) polyesters from ω-hydroxydecoic acid,[49] (8) polymeric ε-hexolactone,[50] (9) polyformals and *super*-polyformals,[51] (10) polydecamethylene oxide,[52] and macrocyclic esters.[53]

The open-chain polyesters from dibasic acids and glycols are microcrystalline solids of molecular weight 800—5000 : these are readily soluble in suitable solvents, their solutions are not highly viscous, and they show no signs of inherent colloidal behaviour. Carothers designates the linear esters of this molecular magnitude α-polyesters. The successive intermolecular couplings which constitute polyesterification are liable to reversal, and at equilibrium an exceedingly large number of entities are involved. The equilibrium can be displaced by the removal of the liberated water, and the more complete the reaction the longer are the molecules of the polyester. Limitation of polyesterification by ring formation does not normally occur.

The limit of polyesterification attained by heating the reactants under reduced pressure (with provision for the removal of the eliminated water) is reached at a molecular weight of about 5000, and progress beyond this point is only attained by very prolonged heating of the α-forms in a molecular still. The products so obtained have molecular weights of over 10,000 (probably in the neighbourhood of 20,000) and have been designated *super*polyesters or ω-forms of polyesters. They are substances of great interest, swelling in solvents, but dissolving only very slowly with formation of highly viscous solutions.

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[41] W. H. Carothers, *J. Amer. Chem. Soc.*, 1930, **52**, 3470; *A.*, 1930, 1272; J. W. Hill, *ibid.*, p. 4110; *A.*, 1930, 1558.

[42] J. W. Hill and W. H. Carothers, *ibid.*, 1932, **54**, 1569; *A.*, 1932, 601.

[43] W. H. Carothers and J. A. Arvin, *ibid.*, 1929, **51**, 2560; *A.*, 1929, 1165; W. H. Carothers, J. A. Arvin, and G. L. Dorough, *ibid.*, 1930, **52**, 3292; *A.*, 1930, 1272; W. H. Carothers and G. L. Dorough, *ibid.*, p. 711; *A.*, 1930, 452; W. H. Carothers and F. J. Van Natta, *ibid.*, p. 314; *A.*, 1930, 319.

[44] J. W. Hill, *ibid.*, 1932, **54**, 4105; *A.*, 1932, 1233.

[45] W. H. Carothers and G. J. Berchet, *ibid.*, 1930, **52**, 5289; *A.*, 1931, 205

[46] W. H. Carothers and J. W. Hill, *ibid.*, 1932, **54**, 1559; *A.*, 1932, 601.

[47] *Idem*, *ibid.*, p. 1566; *A.*, 1932, 601.

[48] W. H. Carothers and J. E. Kirby, *ibid.*, p. 1588; *A.*, 1932, 601.

[49] W. H. Carothers and F. J. Van Natta, *ibid.*, 1933, **55**, 4714; *A.*, 1934, 56.

[50] F. J. Van Natta, J. W. Hill, and W. H. Carothers, *ibid.*, 1934, **56**, 455; *A.*, 1934, 392.

[51] J. W. Hill and W. H. Carothers, *ibid.*, 1935, **57**, 925; *A.*, 844.

[52] J. W. Hill, *ibid.*, p. 1131; *A.*, 1104.

[53] E. W. Spanagel and W. H. Carothers, *ibid.*, p. 929; *A.*, 844.

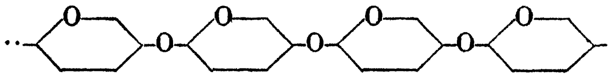
From ε-aminohexoic acid, by heating above its melting point, polyamides of the polymeric series

$$\cdot NH\cdot[CH_2]_5\cdot CO\cdot NH\cdot[CH_2]_5\cdot CO\cdot NH\cdot[CH_2]_5\cdot CO\cdot$$

are formed. These have a molecular weight of at least 1000 (probably actually about 3000) and from them, by further prolonged heating in a molecular still, *super*polyamides can be obtained. By heating together trimethylene glycol, suberic acid, and ε-aminohexoic acid, a *mixed* polyester-polyamide has been obtained and this in turn has been converted into a *super*polyester-polyamide.

The importance attaching to the *super-* or ω-compounds of the polyester, polyamide, and polyester-polyamide classes arises from the ability of these polymerides to furnish strong, pliable, highly oriented fibres. This property is discussed in an interesting paper by W. H. Carothers and J. W. Hill.[54] The fibres from such *super*-polyesters as have been examined, although otherwise suitable for employment as synthetic silk, suffer from the defect of low melting point and a considerable degree of solubility in organic solvents. On the other hand the above-mentioned polyamide is too infusible and insoluble to permit of a satisfactory test of its ability to furnish fibres. Intermediate, however, in physical properties between the polyesters and the polyamide is the mixed polyester-polyamide: the fibres of this substance are strong, pliable, and highly oriented and closely simulate natural silk and cellulose fibres, and also resemble cellulose and silk in the essential details of their molecular structure.* Unlike cellulose and rubber, which are extremely sensitive to degradation by heat, the synthetic linear polyesters (which are formed at 200—250°) are resistant to heat. The constitutive analogies represented by the following are of interest:

(I.)



Cellulose (polyacetal)

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[54] *J. Amer. Chem. Soc.*, 1932, **54**, 1579; *A.*, 1932, 601.

* For Carothers and Hill's view of the physical constitution of a perfectly oriented fibre and the molecular weights (or lengths) at which fibre-strength, pliability, and capacity for cold-drawing appear in useful degree, see the original paper (*loc. cit.*). Besides length of molecule, good crystallising capacity and therefore good orientation are held to be desirable features in obtaining strength and pliability. Three-dimensional polymerides, including glyptal resins, are by their structure likely to be unsuited for fibre orientation, and on test have yielded only fragile (although lustrous) threads with no sign of orientation.

(II.) ·NH·R·CO·NH·R′·CO·NH·R·CO·NH·R′·CO·
Silk (*polyamide*)

·O·R·CO·O·R·CO·O·R·CO·
Polyester (from hydroxy-acid)
(III.)

·O·R·O·CO·R′·CO·O·R·O·CO·R′·CO·
Polyester (from dibasic acid and glycol)
(IV.)

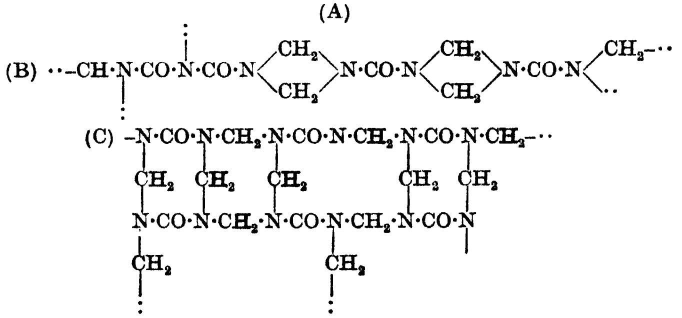
·O·R·CO·NH·R′·CO·NH·R′·CO·O·R·CO·
Mixed polyester-polyamide
(V.)

·O·CO·R·CO·O·CO·R·CO·
Polyanhydride
(VI.)

Resins.—The principles of condensation-polymerisation as described by W. H. Carothers appear from the work of G. Walter [55] to apply to the formation of urea–formaldehyde resins. Resins are generally mixtures of mutually soluble components possessing related structures : * these components may differ in one or all of three characteristics, *viz.*, analytical composition, molecular structure, and molecular size. The majority of urea–formaldehyde resins differ in all three characteristics owing, first, to the different behaviour of the primary products of condensation obtained from urea and formaldehyde at different relative concentrations and under different conditions, and, secondly, to the different possibilities of further condensation (or polymerisation) which those primary products (or their immediate derivatives) present.

The only primary products are stated to be monomethylol urea, $HO{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$, and dimethylol urea, $HO{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OH$: all other products of the reaction can be traced back to them. The probable nature of the components of the resins has been deduced by Walter, and the latter are represented as ranging from methylol-methylene-urea, $HO{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}N{:}CH_2$, through open-chain and ring-compounds

$HO{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}N(CH_2{\cdot}OH){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}N(CH_2{\cdot}OH){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}$
(A)


(B) ···–CH·N·CO·N·CO·N
CH₂
CH₂
N·CO·N
CH₂
CH₂
N·CO·N
CH₂–···
(C) –N·CO·N·CH₂·N·CO·N·CH₂·N·CO·N·CH₂–···
CH₂
N·CO·N·CH₂·N·CO·N·CH₂·N·CO·N
CH₂

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[55] *Trans. Faraday Soc.*, 1936, **32**, 377; compare G. Walter and M. Gewing, *Kolloidchem. Beih.*, 1931, **34**, 163; *A.*, 1932, 156; T. Scheiber and K. Sändig, "Die künstlichen Harze."

* For views regarding the internal structure of resins and amorphous materials, see R. Houwink, *Trans. Faraday Soc.*, 1936, **32**, 123.

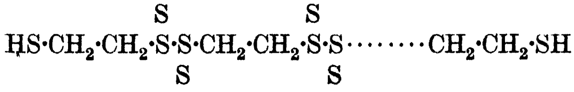
of the types (A) and (B) respectively, to three-dimensional networks such as (C).

Somewhat similar basic reactivities account for the production of insoluble and infusible resins by condensation of arylsulphamides with formaldehyde.[56] Resins of both linear and cyclic structure have been obtained from thiocarbamide, formaldehyde, and cuprous chloride.[57]

An interesting type of multicondensation leading to linear chains of high molecular weight is that which occurs between organic dihalides whose molecules terminate in $\cdot CH_2X$ groups and metallic polysulphides.[58] Specific examples are the following :

$$Cl\cdot[CH_2]_2\cdot Cl + M_2S_x \longrightarrow -[CH_2]_2\cdot S_x\cdot[CH_2]_2\cdot S_x\cdot[CH_2]_2\cdot S_x-$$
$$Cl\cdot[CH_2]_6\cdot Cl + M_2S_x \longrightarrow -[CH_2]_6\cdot S_x\cdot[CH_2]_6\cdot S_x\cdot[CH_2]_6\cdot S_x-$$
$$Cl\cdot C_2H_4\cdot O\cdot C_2H_4Cl + M_2S_x \longrightarrow -C_2H_4\cdot O\cdot C_2H_4\cdot S_x\cdot C_2H_4\cdot O\cdot C_2H_4\cdot S_x-$$

Many of the products, after acidification, are elastic rubbery masses (thiokol resins), and the polymeride from sodium tetrasulphide (Na_2S_4) and ethylene dichloride in particular possesses in good degree extensibility and reactivity, and undergoes a process superficially similar to the vulcanisation of rubber. The polymeric chain, in the latter instance, appears to contain only two atoms of sulphur per unit, the residual sulphur (capable of removal and restoration) being probably co-ordinately bound :



$$HS\cdot CH_2\cdot CH_2\cdot \overset{S}{\underset{S}{S}}\cdot S\cdot CH_2\cdot CH_2\cdot \overset{S}{\underset{S}{S}}\cdot S\cdots\cdots CH_2\cdot CH_2\cdot SH$$

The early work on phenol–formaldehyde condensations indicated that acidic condensations of phenols with formaldehyde generally lead to compounds of dihydroxydiarylmethane type, and that alkaline condensations produce phenolic alcohols. This knowledge was linked with the facts that acidic condensations often yield permanently fusible and soluble resins (novolaks), and that condensations under alkaline conditions generally lead to heat-hardening resins (" bakelite " type). N. J. L. Megson [59] has studied the novolaks on the assumption that they are intermediates in the production of more complex resins and that in consequence a knowledge of the constitution of the former would throw light on that of the latter. Baekeland and Bender had originally regarded the novolaks as possessing a phenoxyhydroxymethane structure, but Megson brings evidence in favour of the following method of building up :

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[56] G. Walter, *Trans. Faraday Soc.*, 1936, **32**, 402.

[57] G. Walter and K. Oesterreich, *Kolloidchem. Beih.*, 1931, **34**, 115; *A.*, 1931, 1398.

[58] *Trans. Faraday Soc.*, 1936, **32**, 347; see also J. R. Katz, *ibid.*, p. 89.

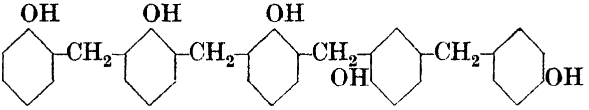
[59] *Ibid.*, p. 336.

$$\mathrm{R{\cdot}OH} \xrightarrow{\mathrm{CH_2O}} \mathrm{HO{\cdot}R'{\cdot}CH_2{\cdot}OH} \xrightarrow{\mathrm{ROH}} \mathrm{HO{\cdot}R'{\cdot}CH_2{\cdot}R'{\cdot}OH} \xrightarrow{\mathrm{CH_2O}} \mathrm{HO{\cdot}R'{\cdot}CH_2{\cdot}R''(OH){\cdot}CH_2{\cdot}OH}, \text{ etc.,}$$

or in general terms,

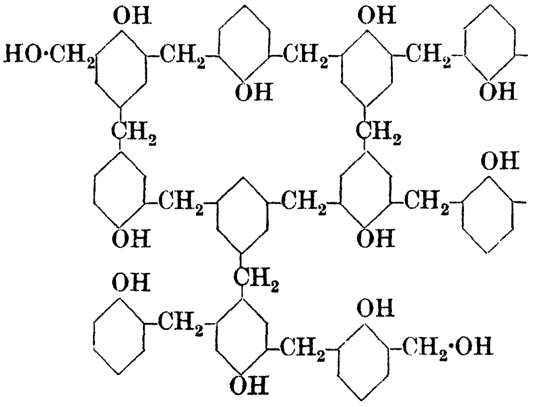
$$x\mathrm{ROH} + (x-1)\mathrm{CH_2O} \longrightarrow \mathrm{HO{\cdot}R'{\cdot}CH_2{\cdot}[R''(OH){\cdot}CH_2]_{x-2}{\cdot}R'{\cdot}OH}$$

The novolaks are then considered to be complex mixtures of essentially linear polymerides of different molecular weights, the complexity due to variation in chain length being greatly increased by the manifest capacity for coupling to take place at both *o*- and *p*-positions of the phenol molecule ; in such a mixture crystallisation of individuals would be difficult. Purely random *o*- and *p*-linking being assumed, a typical product would be constituted as in (A).



(A)

In the formation of more infusible phenol–formaldehyde resins, R. Houwink [60] pictures condensation as proceeding further to give three-dimensional molecules, as in (B), although in this representation no regularity in linking or pattern is intended.



(B)

E. H. F.

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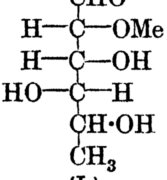
[60] *Trans. Faraday Soc.*, 1936, **32**, 125.

3. Carbohydrates.

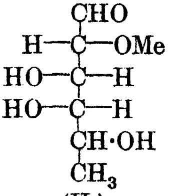
General.—Unabated interest in the chemistry of the carbohydrates continues, and the very large number of papers published serves to indicate the nature and importance of the numerous major problems which still await solution. In the present review it is possible to refer only to a small proportion of the published articles, and the discussion of many, of considerable interest, will be held over until the problems dealt with can be treated as a whole.

Two methods have been used by E. Montgomery and C. S. Hudson[1] for the measurement of the initial rotation of β-*l*-arabinose, both of which give approx. $[\alpha]_D + 201{\cdot}5°$ for the initial value in water. During the course of the work the highly purified β-form was obtained by very slow crystallisation of the sugar from pyridine or aqueous acetone. The mutarotation of arabinose has been studied also by C. N. Riiber and N. A. Sörensen,[2] who give +192° for the initial value and find that the mutarotation is not a unimolecular reaction. In this respect and also as regards molecular solution volume and refraction β-*l*-arabinose and α-*d*-galactose are closely similar, results which are readily understandable when the structural formulæ of the two sugars are compared. The equilibrated solution of arabinose contains not only α- and β-*l*-arabopyranose but also a third form, which has $[\alpha]_D + 46°$ approx. and does not appear to be the aldehyde form.

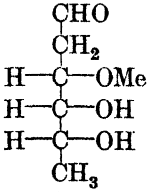
Glucose 2-benzoate, glucose 3-benzoate, and glucose 6-benzoate have been prepared in the course of investigations on the benzoyl derivatives of glucose: the last-named substance is identical with vacciniin, which occurs naturally in cranberries.[3] Further progress has been made in the study of digitalose, the methylated methylpentose which occurs in digitalis glucosides. It has now been found that digitalose gives on oxidation a dibasic acid, which on methylation yields methyl *l*-trimethoxyglutarate. The earlier work of Kiliani appeared to have limited the choice of formula for digitalose



(I.)



(II.)



(III.)

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[1] *J. Amer. Chem. Soc.*, 1934, **56**, 2074; *A.*, 1934, 1337.

[2] *K. Norske Vidensk. Selsk. Skr.*, 1933, No. 7, 1; *A.*, 1934, 1312.

[3] P. Brigl and W. Zerrweck, *Z. physiol. Chem.*, 1934, **229**, 117; *A.*, 1935, 199.

to four possibilities, but these new experiments reveal that none of these can be correct. It is now clear that the configuration of the second, third, and fourth carbon atoms must be represented by either (I) or (II), but the configuration of the fifth carbon atom has not been determined and choice has yet to be made among four possible formulæ for digitalose.[4] Cymarose, a methylated 6-deoxyhexose occurring in strophanthin and other glucosides, gives rise on oxidation with nitric acid to a hydroxymethoxyglutaric acid which forms a lactone. The methoxy-group is therefore on the third carbon atom of the sugar chain and this result, taken in conjunction with the other properties of cymarose, renders it probable that this sugar is 3-methyl digitoxose having the structural formula (III).[5]

The natural colouring matter rutin (a glucoside of quercetin) yields on enzymic hydrolysis the disaccharide rutinose, which has been transformed into its β-hepta-acetate and the corresponding hexa-acetyl β-methylglycoside. The former substance is identical with the synthetic β-hepta-acetate of β-*l*-rhamnosido-6-*d*-glucose and the latter with the synthetically prepared hexa-acetate of the β-methylglycoside of β-rhamnopyranosido-6-*d*-glucopyranose. The constitution of rutinose is therefore clear and it remains only to determine whether the glycosidic link in rutin is α or β.[6]

The constitution of synthetic *iso*sucrose has been investigated by the methylation method. The octamethyl derivative affords on hydrolysis tetramethyl glucopyranose and tetramethyl fructofuranose. The constitution is thereby established and it follows that sucrose and *iso*sucrose differ only in the nature of the glycosidic links.[7]

Investigations into the chemistry of sugars with branched carbon chains have been continued by O. T. Schmidt and his collaborators.[8] The α- and the β-fructoheptonic acid obtained by Kiliani's method when fructose is combined with hydrogen cyanide have been separated and examination of their properties indicates that the α-compound, the nitrile of which was obtained by Kiliani and Düll, is α-hydroxymethyl gluconic acid and that β-fructoheptonic acid is α-hydroxymethyl mannonic acid (IV). *d*-Xyloketose yields similarly α-hydroxymethyl lyxonic acid and α-hydroxymethyl xylonic acid. Experiments with *l*-araboketose and *d*-araboketose yielded analogous products and it was observed that α-hydroxymethyl *d*-ribonic acid

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[4] O. T. Schmidt and H. Zeiser, *Ber.*, 1934, **67**, [*B*], 2127; *A.*, 1935, 200.

[5] R. C. Elderfield, *Science*, 1935, **81**, 440; *A.*, 848.

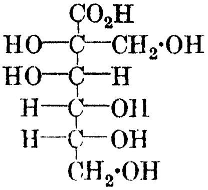
[6] G. Zemplén and A. Gerecs, *Ber.*, 1935, **68**, [*B*], 1318; *A.*, 1109.

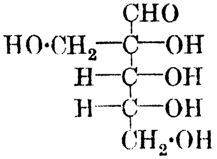
[7] (Sir) J. C. Irvine and D. Routledge, *J. Amer. Chem. Soc.*, 1935, **57**, 1411; *A.*, 1226.

[8] O. T. Schmidt and C. C. Weber-Molster, *Annalen*, 1934, **515**, 43, 65; *A.*, 1935, **196**; **O. T. Schmidt and K. Heintz**, *ibid.*, p. 77; *A.*, 1935, 196.

(from *d*-araboketose) was identical with hamamelonic acid. The sugar hamamelose must be therefore an α-hydroxymethyl *d*-ribose (V).

(IV.)

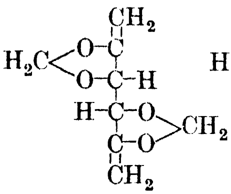




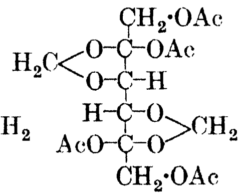
(V.)

On evaporation in the presence of hydrochloric acid, (IV) gives an anhydrolactone in which the anhydro-ring is extremely stable, whereas the corresponding hydroxymethyl gluconic acid does not give rise to an anhydro-compound. During the course of this work the authors examined the action of pyridine on various sugars and, contrary to the statements of previous workers,[9] found that both xyloketose and lyxose were produced when xylose was heated with pyridine. The analysis of mixtures of ketopentoses and aldopentoses is complicated by the fact that the former as well as the latter are readily oxidised by iodine in the presence of potassium bicarbonate.

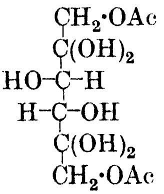
The first example in the sugar series of a diketose has been prepared by F. Micheel and K. Horn,[10] who transformed 1 : 6-di-iodo-2 : 3 : 4 : 5-dimethylene mannitol into the corresponding 1 : 2 : 5 : 6-diene (VI). The diene when oxidised by lead tetra-acetate gives the tetra-acetate (VII), which yields on gentle hydrolysis the 1 : 6-diacetate of 5-ketofructose (5-fructonose) in the form of its dihydrate (VIII). On removal of the acetyl groups by Zemplén's method 5-ketofructose (5-fructonose) (IX) is obtained. The diketose reduces Fehling's solution instantly in the cold, forms crystalline phenylhydrazones and osazones, and possesses the remarkable property of being fermentable by yeast, a characteristic it shares exclusively in the monose series with the trioses *d*-glyceraldehyde and dihydroxyacetone and with the naturally occurring



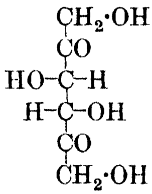
(VI.)



(VII.)



(VIII.)



(IX.)

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[9] P. A. Levene and D. W. Hill, *J. Biol. Chem.*, 1933, **102**, 563; *A.*, 1933, 1278.

[10] *Annalen*, 1934, **515**, 1; *A.*, 1935, 200.

hexoses *d*-glucose, *d*-fructose, *d*-mannose, and *d*-galactose. The reasons underlying this behaviour are as yet little understood and the results of further investigations will be awaited with interest.

The use of liquid ammonia as a reagent in sugar chemistry is being explored. For example, certain amides which cannot be obtained by the usual procedure are readily prepared by the action of liquid ammonia on the lactone of the acid.[11] The action of the reagent on free sugars is more complicated. L. Zechmeister and G. Tóth [12] have found that deacetylation of cellobiose octa-acetate can be effected by treatment with liquid ammonia at 50°, but the principal product consists of cellobiose residues linked together through a nitrogen atom. I. E. Muskat [13] reports that carbohydrates containing free or potential aldehyde or ketone groups are readily oxidised by iodine in liquid ammonia, the product formed from the aldose being the amide of the corresponding aldonic acid. The same author describes in detail the apparatus and methods by which the potassium derivatives of certain carbohydrates, *e.g.*, glucose diacetone, can be prepared by the action of the metal on the sugar derivative dissolved in liquid ammonia. The metallic atom can then be replaced, usually in good yield, by methyl, ethyl, etc., or, if the appropriate acyl chloride is utilised, by acyl groups. The method may also be used in the preparation of derivatives such as tri(glucose diacetone) arsenite.

Special interest is attached to the cyclic alcohols in view of the action of *meso*-inositol as a growth-promoting factor in the Bios group. Nevertheless, little is known concerning the transformation of hexoses into the cyclic alcohols. The simple change by aldol condensation of the groups attached to C_1 and C_6, which may possibly take place in the living organism, cannot be brought about *in vitro* and a direct solution of the problem is yet to come. On this account the results recorded by F. Micheel, H. Ruhkopf, and F. Suckfüll [14] are of particular interest. These authors have studied the action of acetic anhydride and zinc chloride on 6-iodo-2 : 3 : 4 : 5-tetra-acetyl aldehydo-*d*-galactose. The main product is hepta-acetyl aldehydo-*dl*-galactose (the first example of its kind of this class of sugar derivative), giving on hydrolysis *dl*-galactose. No simple explanation of the change is available. Direct racemisation and the series of changes involving reduction at C_1 and oxidation at C_6 may be ruled out, and the authors consider it most probable that the following changes are involved in which the re-opening of the ethylene oxide ring must necessarily yield derivatives of *dl*-galactose.

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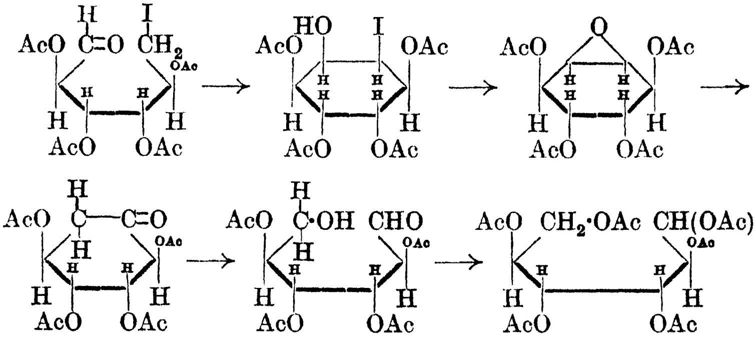
[11] J. W. E. Glattfeld and D. Macmillan, *J. Amer. Chem. Soc.*, 1934, **56**, 2481; *A.*, 1935, 72.

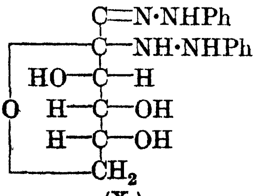
[12] *Naturwiss.*, 1935, **23**, 35; *A.*, 330.

[13] *J. Amer. Chem. Soc.*, 1934, **56**, 2449; *A.*, 1935, 68.

[14] *Ber.*, 1935, **68**, [*B*], 1523; *A.*, 1225.



It has long been suspected that osazones must possess some kind of ring structure, but no certain information has been available concerning the type of ring system or the number of rings involved. Progress towards the solution of this problem is forthcoming from a study of the methylation products of glucosazone. On treatment with methyl sulphate and alkali, glucosazone gives 5-methyl glucosazone and under more vigorous conditions a trimethyl derivative. Removal of the phenylhydrazine residues from the latter by hydrochloric acid yields 3 : 4 : 5-trimethyl glucosone. The latter is reduced to a trimethyl fructose, from which 1 : 3 : 4 : 5-tetramethyl fructopyranose is obtainable. The trimethyl fructose does not give rise to a methylfructofuranoside and in it, therefore, the hydroxyl attached to C_6 is free whereas the hydroxyl on C_5 is methylated. The facts cited are most readily interpreted on the basis of the structure shown in (X) for glucosazone, which appears to possess the ring system present in fructopyranose.[15] In this connexion the work of O. Diels and R. Meyer on anhydro-osazones may be cited.[16] These authors find that under a variety of conditions, for instance, on boiling with alcohol containing some sulphuric acid, *d*-glucosazone is readily converted into 3 : 6-anhydro-*d*-glucosazone. Anhydro-derivatives are similarly obtainable from galactosazone, lactosazone, and maltosazone, and



(X.)

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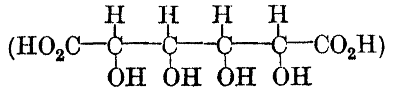
[15] (Mrs.) E. E. Percival and E. G. V. Percival, *J.*, 1935, 1398. The open-chain structure is supported by L. L. Engels (*J. Amer. Chem. Soc.*, 1935, **57**, 2419), who compares the absorption spectra of various osazones.

[16] *Annalen*, 1935, **519**, 157; *A.*, 1225.

since these anhydro-substances have well-defined melting points they are very suitable for identification purposes.

Investigation of the action of barium hypobromite on glucose has revealed that the main product is not 2-ketogluconic acid, as was claimed by F. Hönig and M. Tempus,[17] but consists chiefly of *l*-sorburonic acid (5-keto-*d*-gluconic acid), only traces of the former substance being produced.[18] The strongly reducing substance found when the electrolytic oxidation of glucose by nascent bromine is unduly prolonged has now been identified as 5-ketogluconic acid, the attack on the secondary alcoholic group at C_5 being of special interest in view of the known tendency of certain biological oxidations to proceed easily at C_5.[19]

Although all the sixteen possible aldohexoses have now been obtained (see last year's Report) it appears that the dibasic acid corresponding to allose  $(HO_2C-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CO_2H)$ is not yet known. The inactive dibasic acid which Fischer obtained by epimerisation of mucic acid and which was considered by him to be *allo*-mucic acid has been shown by T. Posternak[20] to be an equimolecular mixture of *d*- and *l*-talomucic acid, produced by epimerisation at one only of the α-C atoms of mucic acid.

Condensation of Sugars with Carbonyl Compounds.

The acetone compounds of the sugars are being increasingly employed as a means of achieving the preparation of partly substituted derivatives (acetates, benzoates, methyl ethers, and others), which in turn are required for syntheses of various types. Moreover, the analogous condensation products of the sugars with benzaldehyde, furfuraldehyde, and paraldehyde are being submitted to closer study for a similar reason.

It would seem that condensation of acetone with monosaccharides usually, but not always, involves *cis*-hydroxyl groups at contiguous carbon atoms. Further, in the condensation of acetone with the free sugar, a readjustment of the pyranose to the furanose form will occur when such a transformation makes available two *cis*-hydroxyl groups. Thus, *d*-galactopyranose (XI) and *d*-fructopyranose (XII) both form diacetone derivatives in which the pyranose ring is retained, the *iso*propylidene groups being attached at contiguous carbon atoms with *cis*-hydroxyl groups, namely, at 1 : 2-3 : 4 in the case of galactose and at 1 : 2-4 : 5 or at 2 : 3-4 : 5 in the case of fructose. *d*-Glucopyranose (XIII) and *d*-mannopyranose (XIV) do not have available two pairs of *cis*-hydroxyl groups and in these cases the diacetone compounds formed are furanose derivatives, namely, 1 : 2-5 : 6-di*iso*propylidene *d*-glucofuranose and

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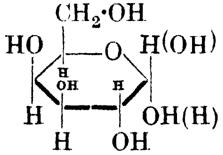
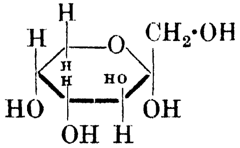
[17] *Ber.*, 1924, **57**, [*B*], 787; *A.*, 1924, i, 712.

[18] T. Reichstein and O. Neracher, *Helv. Chim. Acta*, 1935, **18**, 892; *A.*, 1107.

[19] E. W. Cook and R. T. Major, *J. Amer. Chem. Soc.*, 1935, **57**, 773; *A.*, 732.

[20] *Naturwiss.*, **1935**, **23**, **287**; *A.*, **846**.


(XI.)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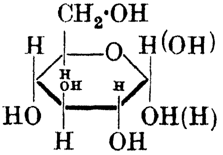
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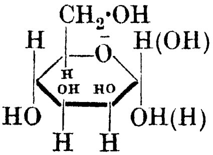
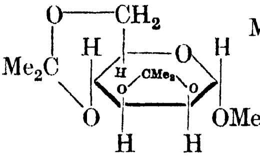
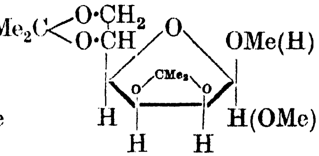

(XIV.)


(XV.)


(XVI.)

2 : 3-5 : 6-di*iso*propylidene *d*-mannofuranose. It has recently been shown that *d*-talose condenses with acetone in a manner entirely analogous to that of mannose.[21] When such ring-change in glucose is precluded by the conditions of the experiment (as, for instance, when the methylglucopyranoside is used instead of the free sugar), no condensation takes place, but that this is not an invariable rule is shown by the fact that a diacetone derivative can be formed from either α- or β-methylmannopyranoside.[22] When α-methylmannopyranoside is treated with acetone (free from methyl alcohol) in the presence of hydrogen chloride, there is formed 2 : 3-4 : 6-di*iso*propylidene α-methylmannopyranoside (XV) together with some 2 : 3-*iso*propylidene α-methylmannopyranoside. It is further observed that, if the acetone contains methyl alcohol, hydrolysis of the glucosidic group becomes possible and ring-change occurs with the production of a mixture containing 2 : 3-5 : 6-di*iso*-propylidene methylmannofuranoside (XVI). In the latter case, "all the conditions which are well recognised as establishing ring-change are present, inasmuch as the general method of introducing ring-shift is to mix a sugar or its glycoside with methyl alcohol in the presence of hydrogen chloride. Under these conditions an equilibrium mixture of α- and β-forms of pyranoside and furanoside is produced."

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[21] W. Bosshard, *Helv. Chim. Acta*, 1935, **18**, 482; *A.*, 734.

[22] R. G. Ault, W. N. Haworth, and E. L. Hirst, *J.*, 1935, 1012; *A.*, 1108.

Taking a broad view, it would seem that acetone condenses more easily with *cis*-hydroxyl groups on contiguous carbon atoms. But that it is not entirely a matter of the spatial arrangement of such groups is clear when it is realised that several forms, both *cis* and *trans*, of the pyranose ring are possible in which the hydroxyl groups at C_4 and C_6 are brought into such spatial proximity as to be equivalent to a pair of *cis*-hydroxyl groups. We have seen that acetone can condense in the case of α-methyl mannoside with two such hydroxyl groups which are not attached to contiguous carbon atoms, and earlier examples of the same phenomenon are presented by 1 : 2-3 : 5-di*iso*propylidene xylofuranose,[23] 1 : 2-3 : 5-di*iso*propylidene glucofuranose (*iso*diacetone-glucose),[24] and 2 : 3-4 : 6-di*iso*propylidene *l*-sorbofuranose.[25]

In contradistinction to the normal course of acetone condensation, we find that with aldehydes the substituted methylene ether most readily formed is that with a six-membered ring, and not the five-membered ring involving contiguous carbon atoms. Thus, the condensation of benzaldehyde with glucose yields 4 : 6-monobenzylidene glucopyranose (XVII).[26] Moreover, benzaldehyde, unlike acetone, will condense with α- and β-methylglucopyranosides to give the corresponding 4 : 6-benzylidene methylglucosides.[27] Although condensation of benzaldehyde with glucose does not facilitate a rearrangement to the furanose form, the aldehyde will condense with glucose derivatives in which the furanose ring is preformed; *e.g.*, with 1 : 2-*iso*propylidene glucofuranose there are obtained two products according to the conditions of the experiment, namely, 1 : 2-*iso*propylidene 3 : 5-benzylidene glucofuranose (XVIII)[28] and 1 : 2-*iso*propylidene 5 : 6-benzylidene glucofuranose (XIX).[29] The first is formed exclusively when the conditions are mild, a higher temperature being necessary for the formation of (XIX). The free terminal group in the 3 : 5-benzylidene compound (XVIII) is easily oxidised to carboxyl, and the compound is therefore valuable as a source of glycuronic acid.[30] It is to be noted that galacturonic and mannuronic acids may be similarly prepared from

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[23] W. N. Haworth and C. R. Porter, *J.*, 1928, 611; *A.*, 1928, 509.

[24] H. Ohle and L. von Vargha, *Ber.*, 1929, **62**, [*B*], 2425; *A.*, 1929, 1279.

[25] T. Reichstein and A. Grüssner, *Helv. Chim. Acta*, 1934, **17**, 311; *A.*, 1934, 511.

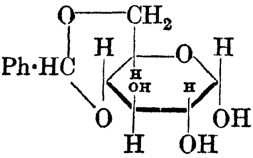
[26] L. Zervas, *Ber.*, 1931, **64**, [*B*], 2289; *A.*, 1931, 1275.

[27] K. Freudenberg, H. Toepffer, and C. C. Anderson, *Ber.*, 1928, **61**, 1750; *A.*, 1928, 1223; H. Ohle and K. Spencker, *ibid.*, p. 2387; *A.*, 1929, 50.

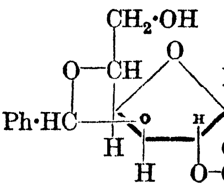
[28] P. Brigl and H. Grüner, *Ber.*, 1932, **65**, [*B*], 1428; *A.*, 1932, 1115.

[29] P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, 1923, **57**, 319; *A.*, 1924, i, 14; P. A. Levene and A. L. Raymond, *Ber.*, 1933, **66**, [*B*], 384; *A.*, 1933, 378.

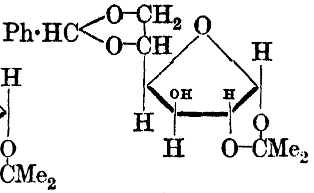
[30] L. Zervas and P. Sessler, *Ber.*, 1933, **66**, [*B*], 1326; *A.*, 1933, 1143.



(XVII.)



(XVIII.)



(XIX.)

3 : 4-di*iso*propylidene α-methylgalactopyranoside[22] and 2 : 3-di*iso*propylidene α-methylmannopyranoside respectively,[31] and 2 : 3-4 : 6-di*iso*propylidene *l*-sorbose has been employed for the preparation of 2-ketogulonic acid.[25]

In the few cases in which it has been studied, it would appear that acetaldehyde more nearly resembles benzaldehyde than it does acetone in its condensation with the sugars. For instance, it condenses with glucopyranose without inducing a change to furanose, to give 4 : 6-ethylidene α-*d*-glucopyranose,[32] analogous to the 4 : 6-benzylidene compound. Nevertheless, acetaldehyde, like benzaldehyde, is capable of condensing at contiguous carbon atoms to form a five-membered methylene ether ring, a fact that is illustrated by the existence of triethylidene sorbitol.[33] Both this substance and 2 : 4-benzylidene sorbitol[34] have been utilised for the preparation of *l*-xylose. It is of interest to note also that ethylidene in 2 : 3-dimethyl 4 : 6-ethylidene β-methylglucopyranoside may be completely replaced by benzylidene by treatment with benzaldehyde in the presence of zinc chloride.[32] Yet another aldehyde has recently been shown to condense to give primarily a six-membered methylene ether ring. This is furfuraldehyde, which reacts with α-methylglucopyranoside to form the 4 : 6-monofurfurylidene derivative and with the corresponding mannoside to give 2 : 3-4 : 6-difurfurylidene α-methylmannopyranoside.[35]

Anhydro-sugars and the Walden Inversion in the Sugar Group.

Considerable progress has been made in the past year in the elucidation of the problems connected with the formation and hydrolysis of *p*-toluenesulphonyl derivatives of the sugars. The alkaline hydrolysis of a *p*-toluenesulphonyl sugar ester leads, when a second hydroxyl group is available in the molecule, to the formation of an anhydro-ring, which may then be ruptured by further and more drastic treatment with alkali, with sodium methoxide, or, in a few cases, with acid. A study of the products of such reactions indicates that both the formation of the anhydro-ring from the *p*-toluenesulphonyl compound and the rupture of that ring by alkali are usually each accompanied by a Walden inversion. The following examples illustrate this thesis. 2-Benzoyl-3-*p*-toluenesulphonyl 4 : 6-benzylidene α-methyl-*d*-glucopyranoside is converted by sodium methoxide into 4 : 6-benzylidene 2 : 3-anhydro-α-methyl-*d*-allopyranoside (inversion at C_3), and further action of sodium methoxide on the latter compound opens the anhydro-ring with the formation of a derivative of *d*-altrose (inversion at C_2). Similarly, the corresponding 3-benzoyl-2-*p*-toluenesulphonyl compound yields a 2 : 3-anhydro-*d*-mannoside (inversion at C_2) and then a derivative of *d*-altrose (inversion at C_3).[36] Again, 3-*p*-toluenesulphonyl 1 : 2-*iso*propylidene *d*-fructopyranose (XXII) with aqueous-alcoholic sodium hydroxide gives 1 : 2-*iso*propylidene 3 : 4-anhydro-*d*-psicose (XXIII) (inversion at C_3) and the anhydro-ring of the latter is opened by sodium methoxide to form a derivative of *d*-sorbose (XXIV) (inversion at C_4).[37] 2 : 3-Dibenzoyl-4-*p*-toluenesulphonyl 6-triphenylmethyl α-methyl-*d*-glucopyranoside, treated with alkali, gives a 3 : 4-anhydro-6-triphenylmethyl α-methyl-*d*-galactoside (inversion at C_4), which is hydrolysed by dry hydrogen chloride in acetone to give derivatives of *d*-gulose (inversion at C_3) and of *d*-galactose (no inversion).[38] A similar series of changes appears to occur when 2 : 3 : 6-triacetyl 4-*p*-toluenesulphonyl β-methyl-*d*-glucopyranoside is used.[39] The 3 : 4-anhydro-sugar formed is most probably a *d*-galactose derivative (inversion at C_4) and the ethylene-oxide ring of the latter opens with sulphuric acid to give derivatives of *d*-gulose (inversion at C_3). No trace of galactose could, in this case, be detected, but the *d*-gulose was accompanied by derivatives of *d*-glucose, which implies opening of the ring with inversion at C_4. A similar phenomenon is observed in the case of fructose referred to above. If the 1 : 2-*iso*propylidene 3 : 4-anhydro-*d*-psicose is treated with sodium hydroxide instead of sodium methoxide, then, among the products, although not the chief product, derivatives of *d*-fructose may be detected, which means that Walden inversion has occurred at C_3 when the ethylene-oxide ring opens. In 6-*p*-toluenesulphonyl 1 : 2-*iso*propylidene *d*-glucofuranose, the *p*-toluenesulphonyl group is of course not attached to an asymmetric carbon atom, so we find that treatment of this compound with sodium methoxide gives 5 : 6-anhydro-

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[31] R. G. Ault, W. N. Haworth, and E. L. Hirst, *J.*, 1935, 517; *A.*, 732.

[32] B. Helferich and H. Appel, *Ber.*, 1931, **64**, [*B*], 1841; *A.*, 1931, 1038.

[33] H. Appel, *J.*, 1935, 425; *A.*, 1935, 734.

[34] L. von Vargha, *Ber.*, 1935, **68**, [*B*], 18, 1377; *A.*, 325, 1104.

[35] H. Bredereck, *ibid.*, p. 777; *A.*, 847.

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[36] G. J. Robertson and C. F. Griffith, *J.*, 1935, 1193; *A.*, 1225.

[37] H. Ohle and F. Just, *Ber.*, 1935, **68**, [*B*], 601; *A.*, 735.

[38] J. W. H. Oldham and G. J. Robertson, *J.*, 1935, 685; *A.*, 963.

[39] A. Müller, *Ber.*, 1935, **68**, [*B*], 1094; *A.*, 964.

1 : 2-*iso*propylidene *d*-glucofuranose (no inversion).[40] This 5 : 6-anhydro-glucose is much more labile than 3 : 6-anhydroglucose; it is hydrolysed, for instance, by acid to give glucose. Heated with dilute alkali, it gives a mixture of 1 : 2-*iso*propylidene *d*-glucose (no inversion) and 1 : 2-*iso*propylidene *l*-idose (inversion at C_5).

We see from these examples that alkaline hydrolysis of a *p*-toluenesulphonate leads first to the formation of an ethylene-oxide ring when a hydroxyl group on the vicinal carbon atom is available and that this ring formation is accompanied by a Walden inversion at the carbon atom to which the *p*-toluenesulphonyl radical was originally attached. Further alkali and sometimes acid treatment of this anhydro-sugar opens the ethylene-oxide ring, such opening being accompanied by Walden inversion at one or other of the carbon atoms involved or at both. It is not yet possible to say whether anhydro-ring formation is a necessary concomitant of Walden inversion or whether simple hydrolysis of the toluenesulphonyl group is sufficient to induce inversion. That anhydro-ring formation may be a necessary precursor of inversion is suggested by such facts as the hydrolysis of 3-*p*-toluenesulphonyl diacetone glucose quantitatively to diacetone glucose and of 4-*p*-toluenesulphonyl 6-triphenylmethyl 2 : 3-dimethyl α-methylglucoside; in neither case does inversion occur.[38] On the other hand, the claim is made that certain *p*-toluenesulphonyl derivatives undergo hydrolysis without ring formation but with inversion. For instance, 5-*p*-toluenesulphonyl-2 : 3-*iso*propylidene methyl-*l*-rhamnofuranoside is hydrolysed by alkali to give 2 : 3-*iso*propylidene 6-deoxy methyl-*d*-gulofuranoside (inversion at C_5) and 4-*p*-toluenesulphonyl 2 : 3-*iso*propylidene methyl-*l*-rhamnopyranoside gives 2 : 3-*iso*propylidene 6-deoxy methyl-*l*-talopyranoside (inversion at C_4).[41] In both these cases the possibility of ring formation is excluded. The facts of this inversion are, however, disputed by P. A. Levene and J. Compton,[42] inasmuch as the properties of 6-deoxy-*d*-gulose synthesised by Kiliani's cyanohydrin method are at variance with those of the substance prepared from *l*-rhamnose. It would seem, in the circumstances, that until further experimental evidence is available it cannot be said that there is a clear case in the sugar series of inversion accompanying alkaline hydrolysis of a *p*-toluenesulphonyl group without anhydro-ring formation.

It would appear, from the examples quoted, that when sodium methoxide is employed in the opening of an anhydro-ring, partial methylation occurs, the methoxyl group attaching itself to the carbon atom at which inversion occurs.[36] If we take into account this fact together with the knowledge that the mode of alkaline hydrolysis of a sulphonic ester is represented rather by (XX) than by (XXI),[43] a tentative suggestion as to the mechanism of inversion

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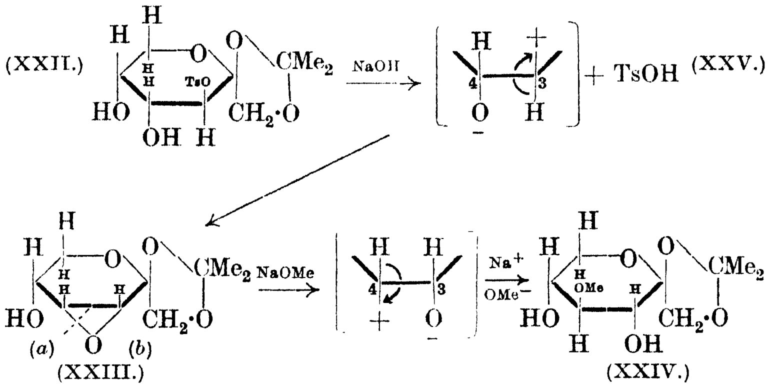
[40] H. Ohle and L. von Vargha, *Ber.*, 1929, **62**, [*B*], 2435; *A.*, 1929, 1279.

[41] I. E. Muskat, *J. Amer. Chem. Soc.*, 1934, **56**, 2653; *A.*, 1935, 199.

[42] *Ibid.*, 1935, **57**, 777; *A.*, 734; I. E. Muskat, *ibid.*, p. 778; *A.*, 734.

$$\text{(XX.)}\quad R{\cdot}SO_2{-}O{-}\vdots{-}R' \qquad\qquad R{\cdot}SO_2{-}\vdots{-}O{-}R'\quad\text{(XXI.)}$$

may be made, taking as an example the conversion of *d*-fructose into *d*-sorbose referred to previously.[37] (In the formulæ, Ts = *p*-toluenesulphonyl.)



The bond which breaks under the influence of sodium methoxide is that marked (*a*) in (XXIII); if it is the bond (*b*) which breaks, then (XXV) should be regenerated and a derivative of *d*-fructose produced. In actual fact a *d*-fructose derivative has been detected among the products of hydrolysis of (XXIII) with aqueous-alcoholic sodium hydroxide.[37]

In most of the examples cited, the anhydro-ring formed is ethylene-oxidic; in many cases this is due to the fact that the only available hydroxyl group is that contiguous to the *p*-toluenesulphonyl group. Nevertheless, it certainly appears that the three-membered anhydro-ring may be formed more readily than a four- or a five-membered ring. In the conversion, for instance, of fructose (XXII) into anhydro-psicose (XXIII), two hydroxyl groups are available, namely, on C_4 and C_5, for anhydride formation when the toluene-sulphonyl group at C_3 is hydrolysed. The oxygen link, however, is formed between C_3 and C_4 and not between C_3 and C_5. Again, we have seen that the alkaline hydrolysis of 6-*p*-toluenesulphonyl 1 : 2-*iso*propylidene *d*-glucofuranose, in which there are unsubstituted hydroxyl groups at C_3 and C_5, gives rise to an ethylene-oxide bridge at positions 5 : 6 and not to the more stable five-membered ring at positions 3 : 6. The 3 : 6-anhydro-ring is only formed when the hydroxyl group at C_5 is protected as in 5 : 6-di-*p*-toluenesulphonyl 1 : 2-*iso*propylidene *d*-glucofuranose. Only the *p*-toluenesulphonyl group at C_6 is removed under the usual conditions of alkaline hydrolysis and the product obtained is 5-*p*-toluenesulphonyl 1 : 2-*iso*propylidene 3 : 6-anhydro-*d*-glucofuranose.[44] It should be noted, however, that, once formed, the 3 : 6-anhydro-ring is more stable to acid and alkaline reagents than is the 5 : 6-compound. An interesting example of a five-membered anhydro-ring is found in the anhydride formed by the alkaline hydrolysis of 4-*p*-toluenesulphonyl 2 : 3 : 6-trimethyl *d*-glucopyranose. It is claimed that this 2 : 3 : 6-trimethyl 1 : 4-anhydro-hexose gives on acid hydrolysis a derivative of *l*-idose, indicating that at some stage Walden inversion has occurred, unexpectedly, at C_5.[45] On the other hand, the 2 : 3 : 6-trimethyl 1 : 4-anhydroglucose prepared by K. Freudenberg and E. Braun [45a] is hydrolysed by acids with formation of 2 : 3 : 6-trimethyl glucose, the latter being unaccompanied by derivatives of idose.

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[43] J. Ferns and A. Lapworth, *J.*, 1912, **101**, 273.

In concluding this section, reference should be made to the use of aluminium chloride in inducing Walden inversion in the sugar series.[46] The effect of this reagent in phosphorus pentachloride on lactose octa-acetate is to produce a disaccharide, neolactose, from which *d*-altrose can be isolated; inversion has therefore occurred at C_2 and C_3 in the glucose moiety. Discrepancies in the published specific rotations of altrose are ascribed to anhydride formation, induced by acids.[47]

Polysaccharides.

Cellulose.—Many papers have appeared in connection with the molecular weight of cellulose and its derivatives. Two of these are concerned with problems of general interest and may be referred to at the beginning of this section. The first is a general review of the chemistry of highly polymerised compounds contributed by H. Staudinger,[48] and the second is a discussion of the meaning of " molecular " (particle) weights of macromolecular substances as determined by different methods.[49] If the molecules of the substance under investigation are not all of the same size, it follows that the particle weight deduced from the usual physico-chemical measurements (a number average) will differ from that given by Staudinger's viscosity method, which gives rather a weight average. Yet a third value, termed by the authors the *Z*-average, can be derived from ultracentrifuge data in addition to the other two. The results emphasise the power and importance of the ultracentrifuge method and their application should give results of exceptional value.

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[44] H. Ohle, L. von Vargha, and H. Erlbach, *Ber.*, 1928, **61**, 1211; *A.*, 1928, 871.

[45] K. Hess and F. Neumann, *Ber.*, 1935, **68**, [*B*], 1360; *A.*, 1109.

[45a] *Ibid.*, p. 1988; *A.*, 1484.

[46] *Ann. Reports*, 1926, 90.

[47] N. K. Richtmyer and C. S. Hudson, *J. Amer. Chem. Soc.*, 1935, **57**, 1716; *A.*, 1355.

[48] *Ber.*, 1935, **68**, [*B*], 1682; *A.*, 1319.

The possibility of break-down of the cellulose chain molecules when dissolved in Schweitzer's reagent has been examined in detail.[50] It is found that, if air and light are rigidly excluded, the cellulose can be recovered with properties unchanged. For ramie cellulose the mean degree of polymerisation determined by the viscosity method in Schweizer's reagent is 900. The initial value is, however, 1300 and the reason for this decrease is not known. In addition, the precise interpretation of viscosity figures obtained in these circumstances is not altogether clear. It is certain, however, from these results and others obtained both viscosimetrically and by osmotic pressure methods that the macromolecules of cellulose are exceedingly large.[51] These conclusions are in agreement with the long-established chemical evidence concerning the structure of cellulose and it becomes all the more obvious that the very low molecular weights postulated by Hess and his collaborators are abnormal phenomena and are not capable of direct interpretation in terms of molecular weight.

Starch, Starch Dextrins, and Glycogen.—The nature of the distinction, physical or chemical, between the amylopectin and the amylose fractions of starch continues to excite attention. A primary difficulty in the way of an elucidation of this problem is one of definition, it being by no means certain that the various " amylopectins " (" α-amyloses ") or " amyloses " (" β-amyloses ") of different authors can be regarded as the same chemical entities. Samec's differentiation of amylose and amylopectin on the basis of electrophoretic separation would appear to ascribe to phosphoric acid a dominant rôle; amylopectin being then simply an amylose esterified with phosphoric acid. But this distinction cannot apply to amylopectins and amyloses prepared in other ways. By treatment with acid ethyl alcohol, potato starch loses entirely its amylopectin character and is converted into a typical amylose without any degradation of the chemical molecule, and the soluble amylose so produced contains the full complement of phosphorus present in the original starch.[52] Similarly, α-amylodextrin, an intermediate product in the enzymic hydrolysis of starch, is found to contain the whole of the phosphorus of the starch, yet it possesses none of the swelling, gel-forming properties of amylopectin. This α-amylodextrin, examined by Haworth's chemical method, is shown to possess a chain length of some 17 glucose units [53] compared with the 26—30 units of undegraded starch, so the actual phosphorus content of the dextrin is nearly double that of potato starch. Further, two dextrins have been prepared from potato starch by heating with glycerol and the molecules are found, again by the chemical method, to consist severally of 10 and 7 glucose units.[54] Despite the fact that these short-chain dextrins still contain phosphorus, they possess none of the properties of amylopectin, nor indeed do they even show the tendency to molecular aggregation displayed by α-amylodextrin. Finally, if it is to be assumed that esterification with phosphoric acid is the basis of the distinction between the two chief constituents of starch, it is very difficult to reconcile the amylopectin content of cereal starches with their phosphorus content, which is generally extremely small. Nevertheless, colloidal starch is negatively charged and this is ascribed to phosphoric acid present as a polysaccharide ester, amylophosphoric acid, which reacts as a dibasic acid.[55] Heated under pressure, the phosphoric ester is gradually hydrolysed and the starch loses its charge. In some starches, as in that of wheat, the conductivity of a solution is less than corresponds to the amount of phosphoric acid present; it is possible that this is due to the presence of basic nitrogen compounds. P. Koets [56] shows that amylose in solution does not form coacervates with positively charged proteins until it has been esterified with phosphoric acid and suggests, on the basis of such observations, that amylopectin is probably a flocculated coacervate of amylophosphoric acid and

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[49] W. D. Lansing and E. O. Kraemer, *J. Amer. Chem. Soc.*, 1935, **57**, 1369; *A.*, 1073; E. O. Kraemer and W. D. Lansing, *J. Physical Chem.*, 1935, **39**, 153; *A.*, 688.

[50] H. Staudinger, B. Ritzenthaler, and (in part) S. Kautz, *Ber.*, 1935, **68**, [*B*], 1225; *A.*, 965.

[51] H. Staudinger, *ibid.*, p. 474; *A.*, 610; H. Staudinger and H. Eilers, *ibid.*, p. 1611; *A.*, 1226; W. Herz, *Cellulosechem.*, 1934, **15**, 95; *A.*, 1934, 1339; B. Obogi and E. Broda, *Kolloid-Z.*, 1934, **69**, 172; *A.*, 1934, 1305; F. Klages, *Annalen*, 1935, **520**, 71; *A.*, 1355; J. Marchlewska, *Rocz. Chem.*, 1935, **15**, 331; *A.*, 1062; H. Staudinger and G. V. Schulz, *Ber.*, 1935, **68**, [*B*], 2320, 2336.

[52] D. K. Baird, W. N. Haworth, and E. L. Hirst, *J.*, 1935, 1201; *A.*, 1226.

[53] W. N. Haworth, E. L. Hirst, and A. C. Waine, *ibid.*, p. 1299; *A.*, 1355.

[54] W. N. Haworth, E. L. Hirst, and (Miss) M. M. T. Plant, *ibid.*, p. 1214; *A.*, 1226.

[55] M. Samec, *Trans. Faraday Soc.*, 1935, **31**, 395; *A.*, 301.

[56] *Proc. K. Akad. Wetensch. Amsterdam*, 1935, **38**, 63; *A.*, 446.

one or more proteins. It is interesting in this connection to note that myosin apparently forms well-defined compounds with starch, in which each molecule of myosin is united with one to ten or more molecules of the polysaccharide.[57] There is a close similarity in physical properties between amylose which has retrograded and amylopectin as it occurs in whole starch. T. C. Taylor and S. G. Morris[58] find that retrograded maize β-amylose (prepared, by freezing, from a clear dispersion of the soluble portion of maize starch) is readily dissolved by cold alkali and is not precipitated from that solution by cold dilute hydrochloric acid. In this way it is distinguished from maize α-amylose (amylopectin), which is also soluble in alkali but is quantitatively precipitated by acid. In maize starch, the α-amylose contains combined fatty acid (4·8%) and this amount is unchanged by solution in alkali and reprecipitation by acid. The suggestion is made that maize β-amylose consists probably of single chains of glucose units hydrated in solution and that "retrogradation" by freezing consists in the partial dehydration of bundles of these chemical units. The process of retrogradation is, in part at least, reversible by prolonged boiling. A. F. Damansky,[59] from a study of the acetylation products, supports the view that potato starch as obtained by extraction is a mixture of Samec's amylopectin and amylose, but regards the amylose as a degradation product of amylopectin; the starch exists in the root entirely as amylopectin. During the transformation of amylopectin into amylose a third hydroxyl group becomes reactive, but the author's suggestion that this change may be due to the fission of a link between glucose molecules is scarcely tenable in view of the results already quoted. Not only are the chemical molecules of the amylopectin and the amylose fractions of potato starch composed of the same number of glucose units, but it is found that the molecules of the starches of various cereals, as, for instance, maize starch and waxy maize starch, approximate in chain length to the same number of glucose units (26—30).[60]

In addition to the dextrin types mentioned above, reference should be made to a renewed investigation of the dextrins of Schardinger. Interest here centres on the nature of the end groups in these crystalline non-reducing oligosaccharides. The number of these dextrins is now increased to five and a study of their hydrolysis supports the view, qualitatively but not quantitatively, that the end groups possess an anhydride structure, possibly of the β-glucosan type.[61]

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[57] S. J. von Przylecki and R. Majmin, *Biochem. Z.*, 1934, **273**, 262; *A.*, 1934, 1374.

[58] *J. Amer. Chem. Soc.*, 1935, **57**, 1070; *A.*, 965.

[59] *Ann. Chim.*, 1934, [xi], **2**, 491; *A.*, 1935, 70.

[60] W. N. Haworth, E. L. Hirst, and (Mrs.) M. D. Woolgar, *J.*, 1935, 177; *A.*, 477.

Investigation of the glycogen from the liver of certain fishes —*Gadidæ*—indicates that this glycogen is very probably identical with that isolated from rabbit-liver. Methylation of the fish-liver glycogen affords a trimethyl glycogen apparently identical with that from rabbit-liver glycogen; both yield on hydrolysis similar amounts of tetramethyl glucopyranose, corresponding with 12 glucose units for the glycogen molecule.[62]

Polysaccharides other than Cellulose, Starch, and Glycogen.—The study of polysaccharides built up of chains of fructose units continues to command attention. The problems involved in this group offer special difficulties in that the hydrolysis products frequently contain a certain proportion of aldose sugar and it is not always clear whether this aldose forms a constituent part of the polysaccharide molecule, is present as an extraneous impurity, or is formed from fructose during the operations involved in the course of hydrolysis. H. H. Schlubach and H. Schmidt [63] have examined inulin from various sources and find slight differences in the rotatory power and rate of hydrolysis. Samples of inulin from Jerusalem artichoke, dahlia, and chicory give only a minute trace of aldose sugar on hydrolysis and before hydrolysis are almost non-reducing. In view of this the authors discuss the nature of the terminal reducing group in the chain in the light of the possibilities outlined by W. N. Haworth, E. L. Hirst, and E. Oliver [64] in their discussion of the fine structure of xylan and other polysaccharides. At present, however, there appears to be no experimental evidence for the aggregation of the macromolecules of inulin, and recent exact measurements of the osmotic pressure of solutions of inulin acetate and methylated inulin by S. R. Carter and B. Record [65] give molecular weights in precise agreement with the value of 30—32 fructofuranose units per molecule, determined by the chemical end-group method. Amongst other polysaccharides based on fructose reference may be made to levosin, which occurs in wheat flour, rye, bran, and stubble. This on hydrolysis appears to yield 1 molecule of glucose to 9 of fructose.[66] On the other hand, graminin, obtained by H. H. Schlubach and K. Koenig[67] from rye, has a rate of hydrolysis similar to that of irisin and appears to be built up entirely of fructofuranose units. Methyl graminin gives on gentle hydrolysis a trimethyl fructofuranose (considered by the authors to be the 3 : 4 : 6-derivative), 1 : 3 : 4 : 6-tetramethyl fructofuranose, and a dimethyl fructose. The three hydrolysis products are present approximately in the proportions 1 : 1 : 1 (or possibly 1 : 2 : 2), the molecular weight of the free polysaccharide is low (approximately 10 units), and for these reasons the authors suggest a structure similar to that of irisin, possibly a ring formed of four fructose residues united through the 1 : 2-positions with other fructose residues attached as side chains.

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[61] K. Freudenberg and R. Jacobi, *Annalen*, 1935, **518**, 102; *A.*, 848.

[62] W. N. Haworth and E. G. V. Percival, *J.*, 1932, 2277; *A.*, 1932, 1022; D. J. Bell, *Nature*, 1935, **136**, 184; *A.*, 1144; *Biochem. J.*, 1935, **29**, 2031; *A.*, 1265.

[63] *Annalen*, 1935, **520**, 43; *A.*, 1354.

[64] *J.*, 1934, 1917; *A.*, 1935, 201.

[65] *Rep. Brit. Assoc.*, 1935; *Nature*, 1935, **136**, 767.

[66] H. Colin and H. Belval, *Bull. Soc. Chim. biol.*, 1935, **17**, 1040; *A.*, 1290.

Several papers dealing with chitin have appeared. Detailed *X*-ray measurements of chitin have been made and an arrangement has been suggested for the chitobiose units in the macromolecules of chitin, the general structure being analogous to that of cellulose.[68] Owing to the difficulty found in swelling chitin, attack by chemical reagents without disruption of the molecule is extremely difficult. Under ordinary conditions acetylation proceeds only to a small extent and when the fully acetylated derivative is made by the aid of hydrogen chloride in acetic anhydride considerable degradation of the macromolecule results.[69] Methylation proceeds even more sluggishly and after 45 treatments with methyl sulphate and alkali the product has only 9% OMe content. After swelling in hydrochloric acid, chitin is methylated somewhat more readily (OMe, 16% after 15 treatments), but again appreciable degradation has occurred.[70] Nitration of chitin dissolved in nitric acid (*d* 1·5) may be effected, and the product esterified to the extent of 1·5 OH groups per C_6 unit has been studied.[71] Attempts to remove the acetyl group in chitin are unsuccessful, in that the amino-group is so protected by the substituent acetyl that degradation invariably occurs. The same authors have studied also the deamination of glucosamine under the conditions adopted by Zechmeister and find that a small amount of the product is different from glucose, mannose, or fructose and they tentatively identify it as chitose.[72]

The view of Ehrlich that pectins contain basic units comprising four galacturonic acid molecules in either ring or open-chain structures is challenged by L. Baur and K. P. Link, who adduce evidence from analysis of the methylglycosides of certain residual polygalacturonic acids that the polygalacturonic acid in question contains approximately 10 uronic acid units.[73]

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[67] *Annalen*, 1934, **514**, 182; *A.*, 1935, 69.

[68] K. H. Meyer and G. W. Pankow, *Helv. Chim. Acta*, 1935, **18**, 589; *A.*, 753.

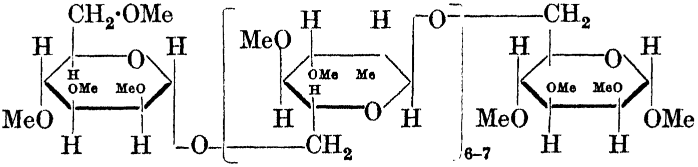
[69] P. Schorigin and E. Hait, *Ber.*, 1935, **68**, [*B*], 971; *A.*, 849.

[70] P. Schorigin and N. N. Makarova-Semljanskaja (with V. Anurjeva), *ibid.*, p. 969; *A.*, 849.

[71] P. Schorigin and E. Hait, *ibid.*, 1934, **67**, [*B*], 1712; *A.*, 1934, 1340.

[72] P. Schorigin and N. N. Makarova-Semljanskaja, *ibid.*, 1935, **68**, [*B*], 965; *A.*, 849.

The first of a series of communications dealing with polysaccharides synthesised by micro-organisms has been published by W. N. Haworth, H. Raistrick, and M. Stacey.[74] This paper is concerned with mannocarolose, a polysaccharide formed, along with many other products,* when *Penicillium Charlesii* G. Smith is grown on Czapek–Dox glucose solutions. On hydrolysis, mannose is the only sugar produced. The iodine number and the viscosity of the acetyl derivative in *m*-cresol solution corresponded to a molecular weight of 9 mannose units. The same value was found by direct gravimetric assay of the end group in the methylated polysaccharide, which yielded on hydrolysis 13% of tetramethyl mannopyranose. It is of interest to find in this instance general agreement of all three methods of determining the molecular size. The principal hydrolysis product from the fully methylated substance was 2 : 3 : 4-trimethyl mannopyranose, the constitution of which was proved by its oxidation in two stages to 2 : 3 : 4-trimethyl δ-mannonolactone and then to *d*-arabotrimethoxyglutaric acid. The simplest representation of the methylated mannocarolose is therefore that shown below, the mannopyranose units being joined together through the 1 : 6-positions by α-glycosidic links. Together with the above-mentioned hydrolysis products, some 10% of 2 : 3-dimethyl mannose was encountered. The origin of this is still not clear. It may arise owing to incomplete methylation, but in view of the fact that the amount approaches that of the tetramethyl mannose isolated, the possibility is conceivable that its isolation has some structural significance and the authors put forward the above formula with this proviso. In view, however, of the reducing



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* These include an interesting series of acids related to γ-methyl tetronic acid, the constitutions of which offer many novel features. The structural formulæ have been assigned by P. W. Clutterbuck, H. Raistrick, and F. Reuter.[75]

[73] *J. Biol. Chem.*, 1935, **109**, 293; *A.*, 732.

[74] *Biochem. J.*, 1935, **29**, 612; *A.*, 477.

[75] *Ibid.*, p., 300, 871, 1300; *A.*, 327, 662, 898.

properties of the polysaccharide its alternative formulation as a continuous loop with a mannose side chain seems highly improbable.

Investigations into the nature of the polysaccharides of yeast have been reported.[76] By prolonged aqueous extraction of suitably treated yeast (*Saccharomyces cerevisiæ*) a polysaccharide fraction can be obtained as a colourless powder, freely soluble in water, giving an opalescent solution. It contains some 9% of acetyl and is hydrolysed by hydrochloric acid, giving glucose. It seems likely from the work now described that the so-called "yeast-gum," "yeast-cellulose," and "yeast-glycogen" of Salkowski are not present in yeast in these forms but are secondary products resulting from the action of alkali.

Methods have been given for the isolation of wood starch in a high degree of purity from the sapwood of English oak and walnut. It appears that these starches closely resemble potato, maize, and other starches in some of their properties, but certain well-marked differences were observed. For example, wood starch appears to contain a uronic acid residue in addition to glucose residues united through α-glucosidic links. The glucose residues form some 90% of the whole and it is suggested that the remainder consists of an aldobionic acid anhydride, possibly a glucose-glycuronic acid derivative. It is possible also that the uronic acid residue may be partly methylated.[77]

As a contrast to the above type of sugar derivative present in certain woods it is of interest to note that from the wood of the European larch a polysaccharide can be extracted which contains no methoxyl and no uronic acid. Mannose and glucose are absent also and on hydrolysis the polysaccharide yields arabinose (12%) and galactose (82%). Its empirical formula is thus $[(C_5H_8O_4)(C_6H_{10}O_5)_6]_n$ and the substance seems to be identical with the polysaccharide obtainable from other larch woods. The iodine number indicates a low molecular weight (approx. 8000).[78]

E. L. H.
S. P.

4. CAROTENOIDS.

Since the last Report,[1] investigations in this field have been to a large extent of a consolidating nature; it may be said that the main features of carotenoid chemistry are now firmly established.[2]

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[76] M. G. Sevag, C. Cattaneo, and L. Maiweg, *Annalen*, 1935, **519**, 111; *A.*, 1280.

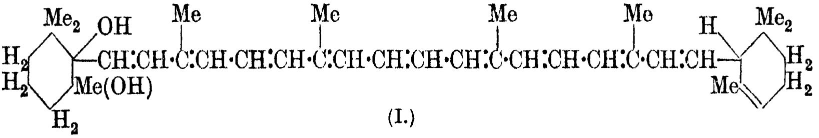
[77] W. G. Campbell, *Biochem. J.*, 1935, **29**, 1068; *A.*, 797.

[78] F. C. Peterson, M. Maugham, and L. E. Wise, *Cellulosechem.*, 1934, **15**, 109; *A.*, 1935, 478.

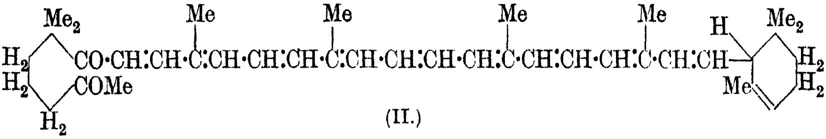
[1] *Ann. Reports*, 1933, **30**, 145.

[2] For detail, see the monograph "Carotenoide," L. Zechmeister, Berlin, 1934.

α-Carotene.—Oxidation of α-carotene with chromic acid gives an α-oxycarotene, $C_{40}H_{58}O_2$,[3] considered to be the α-analogue of β-dihydroxycarotene,[4] and formulated as (I), since it has no vitamin-*A* activity, together with α-semicarotenone (II), $C_{40}H_{56}O_2$, which gives a monoxime only [5] and shows a general correspondence in properties to semi-β-carotenone.[6] It differs from the latter, however, in that it does not exhibit vitamin-*A* activity, indicating that it contains an α- and *not* a β-ionone ring. α-Carotene gives a di-iodide which exhibits vitamin-*A* activity.[3]



(I.)



(II.)

β-*Carotene and Azafrin.*—The symmetrical formula for β-carotene (III) proposed by P. Karrer and his associates [7] has been confirmed by R. Kuhn and H. Brockmann by means of a singularly brilliant series of degradation experiments.[8] Whereas the total structure of lycopene has been established by its degradation to β-norbixin,[9] followed by the synthesis of the perhydro-derivative of the latter,[10] the detailed structure of the polyene chain of β-carotene, in so far as the exact positions of the methyl group attachments are concerned, has hitherto been based mainly upon a high degree of probability.

Mild oxidation of β-carotene with chromic acid yields dihydroxy-β-carotene (IV),[4] the constitution of which has been established by its oxidation with the Criegee reagent to semi-β-carotenone (V). Both dihydroxy-β-carotene and semi-β-carotenone on further oxidation with chromic acid give β-carotenone (VI), which had previously been obtained by the direct oxidation of β-carotene.[6] A probable intermediate in the oxidation of semi-β-carotenone to β-carotenone has been isolated by the mild chromic acid oxidation of dihydroxy-β-carotene, and formulated as dihydroxysemi-β-carotenone (V*a*), since on oxidation with lead tetra-acetate it gives β-carotenone.

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[3] P. Karrer, U. Solmssen, and O. Walker, *Helv. Chim. Acta*, 1934, **17**, 417; *A.*, 1934, 517; P. Karrer, H. v. Euler, and U. Solmssen, *ibid.*, p. 1169; *A.*, 1934, 1221.

[4] R. Kuhn and H. Brockmann, *Ber.*, 1932, **65**, [*B*], 894; 1934, **67**, [*B*], 1408; *A.*, 1932, 749; 1934, 1000; *Annalen*, 1935, **516**, 95; *A.*, 611.

[5] P. Karrer and U. Solmssen, *Helv. Chim. Acta*, 1935, **18**, 25; *A.*, 340.

[6] *Ann. Reports*, 1933, **30**, 152.

[7] P. Karrer, A. Helfenstein, H. Wehrli, and A. Wettstein, *Helv. Chim. Acta*, 1930, **13**, 1084; *A.*, 1930, 1422.

[8] *Annalen*, 1935, **516**, 95; *A.*, 611.

[9] *Ann. Reports*, 1933, **30**, 149.

[10] P. Karrer, P. Benz, R. Morf, H. Raudnitz, M. Stoll, and T. Takahashi, *Helv. Chim. Acta*, 1932, **15**, 1218, 1399; *A.*, 1932, 1234; 1933, 52.

Oxidation of β-carotene under conditions that led to the formation of bixin dialdehyde from lycopene was expected to yield crocetin dialdehyde; this was not the case, however, for a β-carotenone aldehyde, $C_{27}H_{36}O_3$ (VII), was isolated. This aldehyde was also obtained by the further oxidation of either β-carotenone, dihydroxysemi-β-carotenone, semi-β-carotenone, or dihydroxy-β-carotene.

The non-occurrence of isomerides of the first four oxidation products of β-carotene [(IV), (V), (V*a*), (VI)] and the establishment of the function of the oxygen atoms present therein are satisfactory confirmation of the identity and symmetrical distribution of the two ring systems of β-carotene, and the fact that from β-carotene and its first four oxidation products one, and only one, β-carotenone aldehyde is obtained establishes the complete symmetry of the polyene chain of the hydrocarbon. β-Carotenone aldehyde gives four mols. of acetic acid on drastic oxidation (method of R. Kuhn and F. L'Orsa),[11] from which it follows that its polyene chain carries three methyl group attachments, one mol. of acetic acid being ascribed to the terminal acetyl group.

Without making an assumption regarding the location of the methyl group attachments in the polyene chain, it is clear that the formation of β-carotenone aldehyde from either β-carotene or β-carotenone is effected by chain fission between C_3 and C_4 (or between C_{15} and C_{16}). Since β-carotenone aldehyde contains only three methyl group attachments in the polyene chain, it follows that one of the four carotene polyene chain methyl groups is attached between the β-ionone ring A and C_4, and another between the β-ionone ring B and C_{15}.

β-Carotenone aldehyde gives a dioxime with excess and a monoxime with one mol. of hydroxylamine; the latter is a mixture of ketoxime and aldoxime, and gives on dehydration a mixture of unchanged ketoxime and a nitrile, which are separable chromatographically. Controlled hydrolysis of this nitrile gives an amide (VIII), which is identical with anhydroazafrinoneamide prepared from azafrinone [11a] (IX) by successive treatment with thionyl chloride and ammonia, followed by cyclisation of the 1 : 6-diketone system with alkali. β-Carotenone aldehyde is thus the aldehyde of azafrinone and the polyene chain of azafrin [11a] (X) must be identical with part of that of

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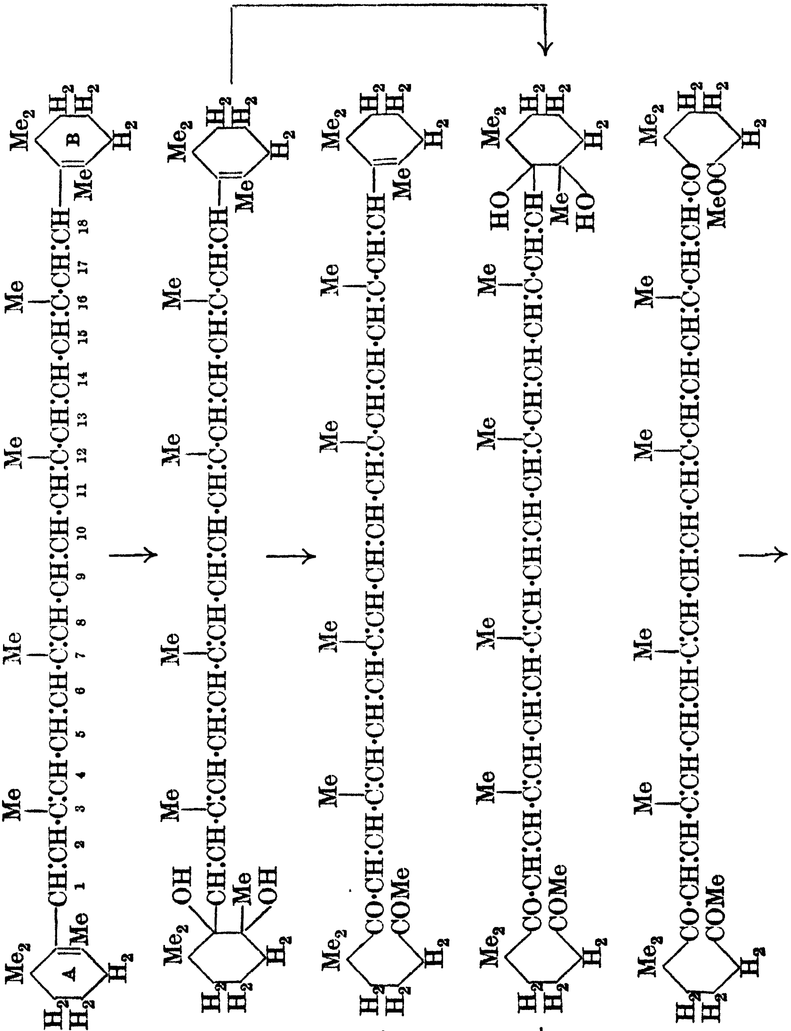
[11] *Z. angew. Chem.*, 1931, **44**, 847; *A.*, 1931, 1437; R. Kuhn and H. Roth, *Ber.*, 1933, **66**, [*B*], 1274; *A.*, 1933, 1179.

[11a] *Ann. Reports*, 1933, **30**, 155.



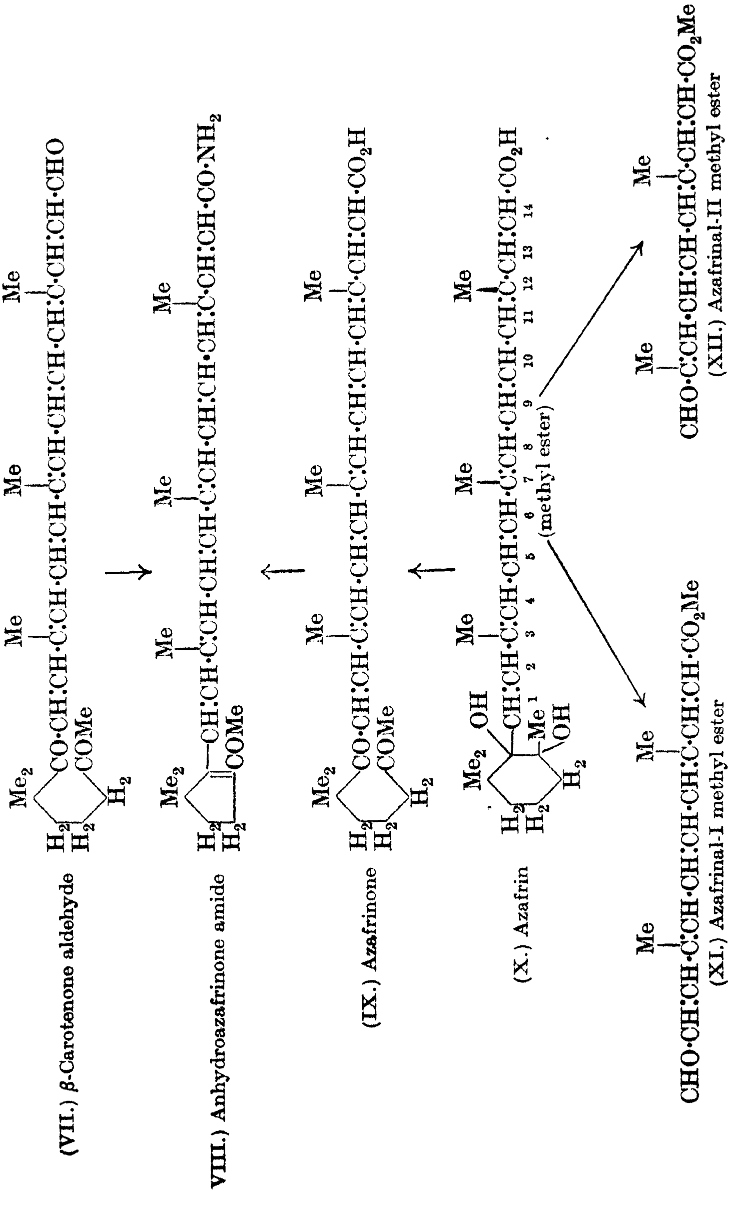
(III.) β-Carotene

(IV.) Dihydroxy-β-carotene

(V.) Semi-β-carotenone

(V*a*.) Dihydroxysemi-β-carotenone

(VI.) β-Carotenone



(VII.) β-Carotenone aldehyde

(VIII.) Anhydroazafrinone amide

(IX.) Azafrinone

(X.) Azafrin (methyl ester)

(XI.) Azafrinal-I methyl ester

(XII.) Azafrinal-II methyl ester

β-carotene; evidence concerning the polyene chain of azafrin can now be directly applied to that of β-carotene.

Oxidation of the methyl ester of azafrin gives a mixture of two aldehyde esters, azafrinal-I methyl ester (XI), $C_{15}H_{18}O_3$, and azafrinal-II methyl ester (XII), $C_{13}H_{16}O_3$, both of which contain two extra-chain methyl groups. The formation of the former is consequent upon rupture of the azafrin polyene chain between C_3 and C_4, and of the latter upon rupture between C_5 and C_6. Since both aldehydes contain only two extra-chain methyl groups, the third extra-chain methyl group of azafrin must be between the ring and C_4, a conclusion in harmony with that arrived at from a consideration of β-carotenone aldehyde. Furthermore, since azafrinal-II is an aldehyde, a methyl group cannot be attached to C_6; so both methyl groups of the azafrinals-I and -II must be attached between C_7 and C_{14}. Thermal decomposition of azafrin gives *m*-toluic acid,[11a] from which it is clear that a methyl group must be attached at either C_{10} or C_{12}, a conclusion necessitating a symmetrically attached methyl group at either C_9 *or* C_7 respectively; *i.e.*, the polyene chain of azafrin has methyl group attachments at either C_9 and C_{10} *or* C_7 and C_{12}. The former arrangement, however, does not allow of the interpretation of the formation of *m*-xylene by thermal decomposition of azafrin; [11a] consequently two methyl groups must be attached to C_{12} and C_7. The formation of *m*-xylene from azafrin now requires that the third methyl group of its polyene chain is attached to C_3. The symmetrical nature of the β-carotene chain locates the remaining extra-chain methyl group at C_{16}; therefore the polyene chain of β-carotene carries methyl group attachments at C_3, C_7, C_{12}, and C_{16}

Xanthophylls.—The so-called caricaxanthin isolated by R. Yamamoto and S. Tin [12] from *Carica papaya* L. has been shown to be kryptoxanthin.[13] Kryptoxanthin is also present in the blooms of the sunflower,[14] in capsicum,[15] and in yellow maize; [16] the vitamin-*A* activity of the last substance is ascribed to its kryptoxanthin content and not to carotene, which is present only in small amount. Cucurbitaxanthin, and cucurbitene,[17] from the giant pumpkin, have likewise proved to be slightly impure lutein and β-carotene respectively.[18]

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[12] *J. Agric. Chem. Soc. Japan*, 1933, **9**, 642; *A.*, 1933, 1343.

[13] P. Karrer and W. Schlientz, *Helv. Chim. Acta*, 1934, **17**, 55; *A.*, 1934, 301.

[14] L. Zechmeister and P. Tuzson, *Ber.*, 1934, **67**, [*B*], 170; *A.*, 1934, 336.

[15] L. Zechmeister and L. v. Cholnoky, *Annalen*, 1934, **509**, 269; *A.*, 1934, 657.

[16] R. Kuhn and C. Grundmann, *Ber.*, 1934, **67**, [*B*], 593; *A.*, 1934, 703.

[17] H. Suginome and K. Ueno, *Bull. Chem. Soc. Japan*, 1931, **6**, 221; *A.*, 1931, 1200.

Rubixanthin.—The ripe hips of the dog rose (*Rosa canina*) contain, in addition to lycopene and carotene, an optically inactive xanthophyll, $C_{40}H_{56}O$, to which the name rubixanthin has been given;[19] the ripe fruits of the species *Rosa rubiginosa* appear to be a particularly suitable source. Rubixanthin is spectroscopically identical with γ-carotene and, like it, gives one mol. of acetone on ozonolysis, and contains twelve ethenoid linkages, thus differing from all previously examined xanthophylls ($11\,|^{=}$). Since the oxygen atom has been diagnosed as a hydroxyl group (Zerewitinoff), it follows that rubixanthin is monocyclic. These observations clearly indicate that rubixanthin is a hydroxy-γ-carotene (XIII) in which the hydroxyl group is situated in the β-ionone ring, since the pure xanthophyll is devoid of vitamin-*A* activity. The depicted position of the hydroxyl group, though highly probable on biogenetic grounds, awaits confirmation.

Zeaxanthin.—Zeaxanthin (from physalien), which has hitherto been anomalous in being the only lævorotatory xanthophyll,[20] has been shown to be optically inactive when carefully purified.[21] Furthermore, this loss of rotatory power is not to be ascribed to racemisation consequent upon the alkaline hydrolysis of physalien, since the naturally occurring ester also is optically inactive and, moreover, the dipalmitate of the purified zeaxanthin is identical with natural physalien. All known xanthophylls are now either dextrorotatory or optically inactive, the latter class comprising kryptoxanthin,[22] zeaxanthin, and rubixanthin.[19] The first two of these are derived from the optically inactive β-carotene by the introduction of one and two hydroxyl groups respectively, whereas the last is a monohydroxy-derivative of the optically inactive γ-carotene. Although asymmetry is thus introduced, the three xanthophylls are optically inactive. Fucoxanthin, previously reported to be dextrorotatory, has recently been shown to be a member of the optically inactive class of xanthophylls;[23] it is not clear, however, to which hydrocarbon it is related. Of the dextro-

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[18] L. Zechmeister and P. Tuzson, *Ber.*, 1934, **67**, [*B*], 824; *A.*, 1934, 710.

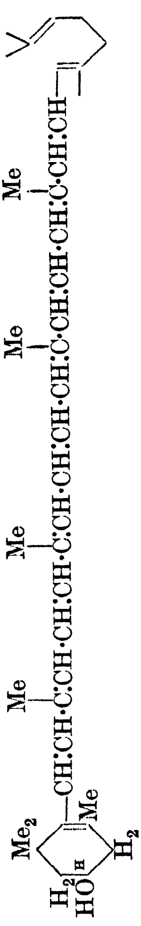
[19] R. Kuhn and C. Grundmann, *ibid.*, pp. 339, 1133; *A.*, 1934, 404, 1047.

[20] P. Karrer, H. Wehrli, and A. Helfenstein, *Helv. Chim. Acta*, 1930, **13**, 268; *A.*, 1930, 609; R. Kuhn, A. Winterstein, and W. Kaufmann, *Ber.*, 1930, **63**, [*B*], 1489; *A.*, 1930, 1044.

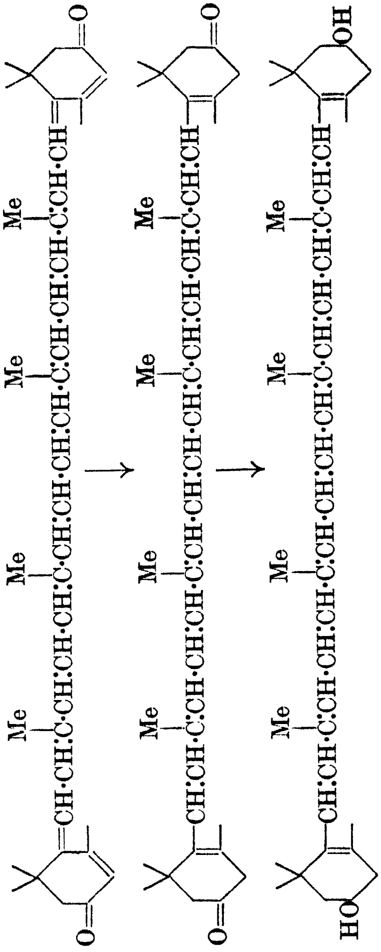
[21] R. Kuhn and C. Grundmann, *Ber.*, 1934, **67**, [*B*], 596; *A.*, 1934, 658.

[22] *Idem*, *Ber.*, 1933, **66**, [*B*], 1746; *A.*, 1934, 70.

[23] I. M. Heilbron and R. F. Phipers, *Biochem. J.*, 1935, **29**, 1369; *A.*, 1040.



(XIII.) Rubixanthin

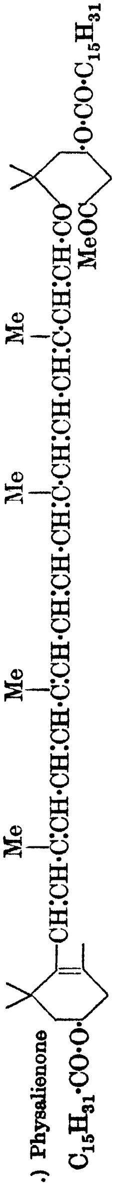


(XIV.) Rhodoxanthin

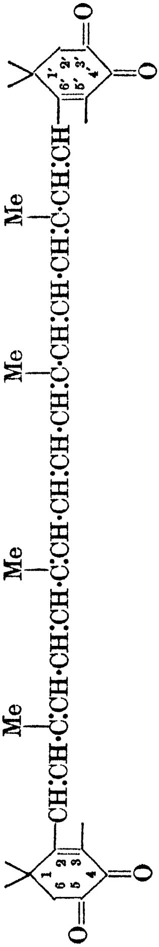
(XV.)

(XVI.) Zeaxanthin

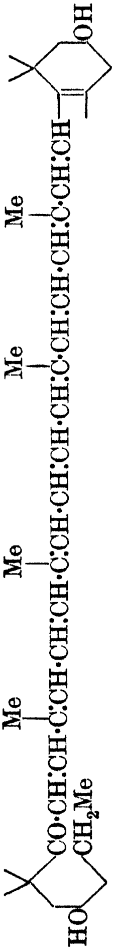
(XVII.) Physalienone



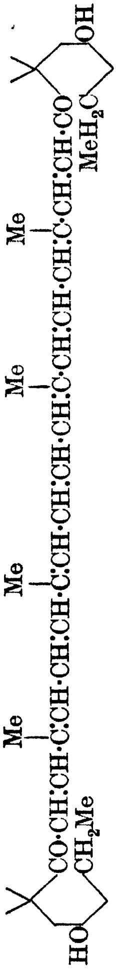
(XVIII.) Astacene



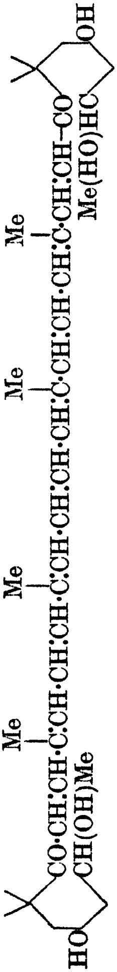
(XIX.) Capsanthin



(XX.) Capsorubin



(XXI.) Fucoxanthin



rotatory xanthophylls, lutein[24] is related to the dextrorotatory α-carotene; it remains to be established to which hydrocarbons the remaining dextrorotatory xanthophylls (flavoxanthin,[25] violaxanthin,[26] and taraxanthin [27]) are related.

The constitutions ascribed to zeaxanthin [20] (XVI) and rhodoxanthin [28] (XIV) have been to a large measure confirmed by the conversion of the latter into the former, a transformation which represents the first artificial conversion of one naturally occurring carotenoid into another. Partial reduction of rhodoxanthin gives a dihydro-derivative [28] (XV), which on treatment with aluminium *iso*propoxide gives zeaxanthin.[29]

Oxidation of zeaxanthin dipalmitate (physalien) gives a diketone, physalienone [3] (XVII), which is spectroscopically similar to semi-β-carotenone and capsanthin, and partial hydrolysis of physalien gives zeaxanthin monopalmitate,[13] the absorption spectrum of which is identical with that of zeaxanthin and of physalien.

Astacene.—Astacene, the carotenoid pigment of lobster (*Astacus gammarus* L.) has been isolated and characterised by R. Kuhn and E. Lederer.[30] It is present as a chromoprotein in the shell and in the ovary and as an ester in the red epidermis. Astacene appears to be the characteristic pigment of the *Crustaceae*; it has been isolated from the eggs of the spider-crab (*Maja-squinada*),[31] from star-fish (*Orphidiaster orphidianus*),[32] from the red skin of the goldfish [33] (*Beryx decadactylus*), from the liver oil of angler fish (*Lophius piscatorius*),[34] from the prawn (*Nephrops norvegicus*),[34] and from whale oil.[34] The salmenic acid of H. v. Euler, H. Hellström, and M. Malmberg [35] has been shown to be astacene.[36]

Astacene has a characteristic absorption spectrum (single broad band, max. 500 mμ in pyridine). The detailed structure of the pigment has been elucidated by P. Karrer and his associates,[37] who established the true molecular formula, $C_{40}H_{48}O_4$, by analysis of astacene dioxime. Since astacene gives a diquinoxaline derivative, it follows that the four oxygen atoms are paired in a di-α-diketone system.

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[24] P. Karrer and A. Zubrys, *Helv. Chim. Acta*, 1933, **16**, 977; *A.*, 1933, 1150.

[25] R. Kuhn and H. Brockmann, *Z. physiol. Chem.*, 1932, **213**, 192; *A.*, 1933, 329.

[26] R. Kuhn and A. Winterstein, *Ber.*, 1931, **64**, 326; *A.*, 1931, 491.

[27] R. Kuhn and E. Lederer, *Z. physiol. Chem.*, 1931, **200**, 108; *A.*, 1931, 1299.

[28] R. Kuhn and H. Brockmann, *Ber.*, 1933, **66**, [*B*], 828; *A.*, 1933, 716.

[29] P. Karrer and U. Solmssen, *Helv. Chim. Acta*, 1935, **18**, 477; *A.*, 754.

[30] *Ber.*, 1933, **66**, [*B*], 488; *A.*, 1933, 509.

[31] R. Kuhn, E. Lederer, and A. Deutsch, *Z. physiol. Chem.*, 1933, **220**, 229; *A.*, 1933, 1318.

[32] P. Karrer and F. Benz, *Helv. Chim. Acta*, 1934, **17**, 412; *A.*, 1934, 531.

[33] E. Lederer, *Compt. rend. Soc. Biol.*, 1935, **118**, 542; *A.*, 646.

[34] G. N. Burkhardt, I. M. Heilbron, H. Jackson, E. G. Parry, and J. A. Lovern, *Biochem J.*, 1934, **28**, 1698; *A.*, 1934, 1246; N. A. Sörensen, *Tidsskr Kjemi Berg.*, 1935, **15**, 12; *A.*, 882.

[35] *Svensk Kem. Tidskr.*, 1933, **45**, 151; *A.*, 1933, 1067.

[36] N. A. Sörensen, *Z. physiol. Chem.*, 1935, **235**, 8.

Astacene exhibits distinct acidic properties which must be ascribed to a keto-enol transformation, since the function of the four oxygen atoms as carbonyl groups is established. This explanation of its acidic nature is confirmed by the observation that the pigment forms a diacetate devoid of acidic properties. The carotenoid contains thirteen easily reducible linkages, of which two are consequent upon enolisation, since perhydroastacene contains two active hydrogen atoms. Astacene is therefore either a 4 : 5 : 4′ : 5′- or a 5 : 6 : 5′ : 6′-tetraketo-β-carotene. The latter form is highly improbable, for according to such a structure the dioxime would certainly be 5 : 5′-dioximino-6 : 6′-diketo-β-carotene and would not be capable of enolisation. Astacene dioxime is, however, completely enolised, containing four active hydrogen atoms (Zerewitinoff), of which two correspond to the oxime residues and two to enolic hydroxyl groups.

Final confirmation of the structure (XVIII) and elimination of the 5 : 6 : 5′ : 6′-tetraketo-β-carotene alternative have been obtained in the isolation of αα-dimethylsuccinic acid from the products of oxidation of the diquinoxaline derivative of astacene.

Capsanthin and Capsorubin.—Red pepper (*Capsicum annuum*) contains a complex mixture of carotenoids, which have been examined with considerable success by L. Zechmeister and L. Cholnoky.[38] In addition to α- (traces only) and β-carotenes, zeaxanthin, lutein, and kryptoxanthin, two new ketonic carotenoids have been isolated by chromatographic methods. The more abundant of these is capsanthin, $C_{40}H_{58}O_3$, and the other, present in small amount only, is capsorubin, $C_{40}H_{60}O_4$.

Catalytic hydrogenation of capsanthin and capsorubin indicates the presence of ten ethenoid linkages and one carbonyl group in the former, and of nine ethenoid linkages and two carbonyl groups in the latter. The remaining two oxygen atoms of both capsanthin and capsorubin are present as easily esterifiable hydroxyl groups. Although capsanthin does not give an oxime, the presence of a carbonyl group has been demonstrated indirectly by the reduction of perhydrocapsanthin with sodium and ethyl alcohol, the number of esterifiable hydroxyl groups then increasing from two to three. The inactivity of the carbonyl group of capsanthin is reminiscent of one of those of semi-β-carotenone. The molecular formula, taken in conjunction with the function of the oxygen atoms and the number of ethenoid linkages, clearly establishes the monocyclic nature of capsanthin and the aliphatic nature of capsorubin.

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[37] P. Karrer and F. Benz, *Helv. Chim. Acta*, 1934, **17**, 412; *A.*, 1934, 531; P. Karrer and L. Loewe, *ibid.*, p. 745; *A.*, 1934, 896; P. Karrer, L. Loewe, and H. Hübner, *ibid.*, 1935, **18**, 96; *A.*, 346.

[38] *Annalen*, 1934, **509**, 269; *A.*, 1934, 657; *ibid.*, 1935, **516**, 30; *A.*, 495.

Since capsanthin does not exhibit vitamin-*A* activity, it cannot contain an unsubstituted β-ionone ring, a conclusion which is confirmed by the observation that on oxidation with permanganate capsanthin gives αα-dimethylsuccinic acid and dimethylmalonic acid but not αα-dimethylglutaric acid.[39]

On this evidence satisfactory formulations have been evolved for capsanthin (XIX) and capsorubin (XX); these structures represent the two carotenoids as stepwise hydration products of zeaxanthin.

Of great interest are the spectroscopic similarities summarised below (maxima in carbon disulphide):

$10\,|^{=} + 1$ terminal $>$CO, all conjugated. $\leftarrow$ Chromophore $\rightarrow$ $9\,|^{=} + 2$ terminal $>$CO, all conjugated.

Capsanthin [38]	542, 503	Capsorubin [38]	541·5, 503, 468
Semi-β-carotenone [40]	538, 499	β-Carotenone [41]	538, 499, 466
Physalienone [3]	538, 503	Bixin dialdehyde [42]	539·5, 502, 467·5

The slight differences in these maxima can be ignored, since L. Zechmeister and L. von Cholnoky record that semi-β-carotenone and capsanthin are spectroscopically indistinguishable in carbon disulphide, ligroin, benzene, or alcohol solution. These spectroscopic data favour the suggested formulæ for the new carotenoids, since according to these structures the change, semi-β-carotenone ⟶ β-carotenone, is identical with the change, capsanthin ⟶ capsorubin, in so far as the chromophoric grouping is concerned.

Fucoxanthin.—The pigment of brown algæ has been obtained in a considerably purer condition than hitherto (see p. 297). The formula $C_{40}H_{56}O_6$ ascribed to fucoxanthin by P. Karrer [39] is abandoned in favour of $C_{40}H_{60}O_6$ by I. M. Heilbron and R. F. Phipers.[23] The carotenoid contains four active hydrogen atoms (Zerewitinoff), but the function of the remaining two oxygen atoms has not been directly established. Although unsuccessful attempts have been made to prepare carbonyl derivatives of the pigment, the presence of such groups is not precluded, since semi-β-carotenone gives a monoxime only and capsanthin fails to give an oxime.

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[39] P. Karrer, A. Helfenstein, H. Wehrli, B. Pieper, and R. Morf, *Helv. Chim. Acta*, 1931, **14**, 614; *A.*, 1931, 733.

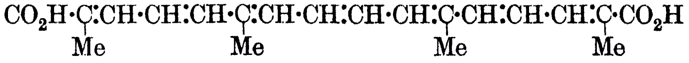
[40] R. Kuhn and H. Brockmann, *Ber.*, 1933, **66**, 1319; *A.*, 1933, 1297.

[41] *Idem, ibid.*, 1932, **65**, 898; *A.*, 1932, 749.

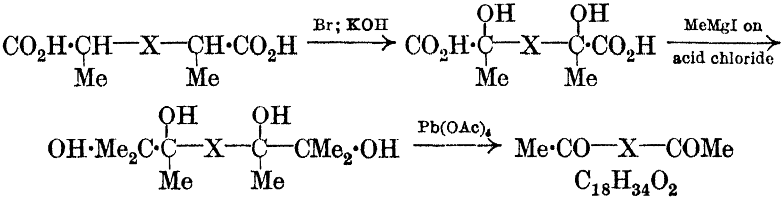
[42] R. Kuhn and C. Grundmann, *Ber.*, 1932, **65**, [*B*], 1880; *A.*, 1933, 142.

Whereas the living *Fucus vesiculosus* contains β-carotene and fucoxanthin, the dead material contains β-carotene and zeaxanthin. No trace of the last pigment could be detected in the fresh algæ; it is suggested that a *post-mortem* transformation, fucoxanthin ⟶ zeaxanthin, occurs. The provisional structure (XXI), which allows of such a transformation to zeaxanthin, has been suggested for fucoxanthin.

Crocetin.—It was reported in 1933 that the constitution of crocetin, the pigment of saffron, had been established as (XXII) and that perhydrocrocetin on degradation according to the following scheme gave a diketone, $C_{18}H_{34}O_2$.

(XXII.) 

$$CO_2H\cdot\underset{Me}{C}{:}CH\cdot CH{:}CH\cdot\underset{Me}{C}{:}CH\cdot CH{:}CH\cdot CH{:}\underset{Me}{C}\cdot CH{:}CH\cdot CH{:}\underset{Me}{C}\cdot CO_2H$$



$$CO_2H\cdot\underset{Me}{CH}-X-\underset{Me}{CH}\cdot CO_2H \xrightarrow{Br;\ KOH} CO_2H\cdot\overset{OH}{\underset{Me}{C}}-X-\overset{OH}{\underset{Me}{C}}\cdot CO_2H \xrightarrow[\text{acid chloride}]{\text{MeMgI on}}$$

$$OH\cdot Me_2C\cdot\overset{OH}{\underset{Me}{C}}-X-\overset{OH}{\underset{Me}{C}}-CMe_2\cdot OH \xrightarrow{Pb(OAc)_4} \underset{C_{18}H_{34}O_2}{Me\cdot CO-X-COMe}$$

This diketone has now been synthesised by P. Karrer and J. Lee [43] by the depicted route, which confirms its structure as 6 : 11-dimethylhexadecane-2 : 15-dione (XXIII).

$$EtO_2C\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2Et \xrightarrow{Na + EtOH}$$

$$CH_2(OH)\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH \xrightarrow{Na;\ EtI}$$

$$CH_2(OEt)\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH \xrightarrow{PBr_3;\ Na}$$

$$CH_2(OEt)\cdot CH_2\cdot CHMe\cdot[CH_2]_4\cdot CHMe\cdot CH_2\cdot CH_2\cdot OEt \xrightarrow[\text{(hydrol.)}]{HBr;\ CHNa(CO_2Et)_2}$$

$$HO_2C\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_4\cdot CHMe\cdot[CH_2]_3\cdot CO_2H \xrightarrow[\text{acid chloride}]{\text{MeZnI on}}$$

$$Me\cdot CO\cdot[CH_2]_3\cdot CHMe\cdot[CH_2]_4\cdot CHMe\cdot[CH_2]_3\cdot COMe \quad \text{(XXIII.)}$$

An interesting thermal degradation of (*trans*-)crocetin dimethyl ester is described by R. Kuhn and A. Winterstein.[44] In addition to *m*-xylene and toluene the reaction leads to the formation of a dimethyl ester, $C_{15}H_{20}O_4$, which contains four ethenoid linkages and three extra-chain methyl groups. The constitution (XXIV), which is in harmony with its spectroscopic properties, has been ascribed to this ester and the mechanism of the reaction is formulated as follows :

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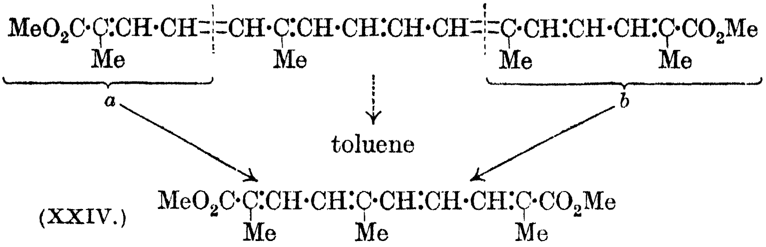
[43] *Helv. Chim. Acta*, 1934, **17**, 545; *A.*, 1934, 635.

[44] *Ber.*, 1933, **66**, 1733; *A.*, 1934, 57.



$$\mathrm{\underbrace{MeO_2C\cdot\underset{Me}{C}{:}CH\cdot CH{=}}_{a}\,\vdots\,{=}CH\cdot\underset{Me}{C}{:}CH\cdot CH{:}CH\cdot CH{=}\,\vdots\,\underbrace{{=}\underset{Me}{C}\cdot CH{:}CH\cdot CH{:}\underset{Me}{C}\cdot CO_2Me}_{b}}$$

$$\downarrow\ \text{toluene}$$

$$\text{(XXIV.)}\quad \mathrm{MeO_2C\cdot\underset{Me}{C}{:}CH\cdot CH{:}\underset{Me}{C}\cdot CH{:}CH\cdot CH{:}\underset{Me}{C}\cdot CO_2Me}$$

It is remarkable that esters of the type *a—a* and *b—b* were not formed.

General.

Several new carotenoids have been isolated and characterised during the period under review. From the sea urchin (*Echinus esculentus*), a pigment pentaxanthin, $C_{40}H_{56}O_5$, has been isolated;[45] it resembles lutein in its absorption spectrum. From the sex glands of the same species, a pigment echinenone, $C_{40}H_{56}O$, has been characterised by its absorption maxima at 520, 488, and 450 mμ (carbon disulphide).[45] A new pigment which exhibits the typical lycopene spectrum has been isolated from *Solanum dulcamara*; it is differentiated from lycopene, however, in its melting point.[46]

The sea anemone, *Actinia equina*, contains an ester, actinioerythrin,[47] which on hydrolysis gives a carotenoid, violaerythrin, characterised by its absorption maxima (carbon disulphide) at 625, 576, and 540 mμ.[48] The red pigment of the *Actinoloba dianthus* species gives on hydrolysis an acidic carotenoid, probably identical with astacene. The species *Anemonia sulcata* contains no esterified pigments, the main lipochrome being sulcataxanthin ($C_{40}H_{52}O_8$?),[48] characterised by three absorption maxima at 516, 482, and 450 mμ (carbon disulphide).

The red anthers of the tiger lily contain, in addition to capsanthin (as an ester), a new xanthophyll ester, hydrolysis of which gives the xanthophyll antheraxanthin ($C_{40}H_{58}O_3$ or $C_{40}H_{56}O_3$),[49] approximating closely in its absorption spectrum to zeaxanthin.

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[45] E. Lederer, *Compt. rend.*, 1935, **201**, 300; *A.*, 1145.

[46] L. Zechmeister and L. v. Cholnoky, *Naturwiss.*, 1935, **23**, 407; *A.*, 983.

[47] R. Fabre and E. Lederer, *Bull. Soc. Chim. biol.*, 1934, **16**, 105; *A.*, 1934, 676.

[48] I. M. Heilbron, H. Jackson, and R. N. Jones, *Biochem. J.*, 1935, **29**, 1384; *A.*, 1005.

[49] P. Karrer and A. Oswald, *Helv. Chim. Acta*, 1935, **18**, 1303.

Three new carotenoid pigments (tabulated below) have been isolated from purple bacteria by P. Karrer and U. Solmssen.[50]

		Max. in CS_2.		
Rhodoviolascin	oxygenated	573·5	534	496
Rhodopin		547	508	478
Rhodopurpurin	$C_{40}H_{56}$ or $C_{40}H_{58}$	550	511	479

From the spectroscopic properties, it is inferred that rhodopurpurin must contain at least thirteen ethenoid linkages and, further, that rhodoviolascin and rhodopin are derivatives of rhodopurpurin. Both rhodoviolascin and rhodopurpurin are epiphasic in spite of a relatively high oxygen content, from which it is suggested that little, if any, of the total oxygen is present as hydroxyl, since xanthophylls with two hydroxyl groups are, in general, hypophasic. F. S. S.

5. Carbocyclic Compounds.[1]

The discovery of large carbon rings and of stable *trans*-dicyclic compounds has led to a revision of our ideas on alicyclic stereochemistry and the strain theory.[2] The first of these topics has been reviewed in these Reports[3] and a few further developments of interest may be noted.

The value for the heat of combustion of the methylene group contained in large carbon rings has been found by L. Ruzicka and P. Schläpfer[4] to lie between 156 and 157 kg.-cals., which is supported by a value independently found for *cyclo*decane.[5] This corresponds with the most accurate recent figure, 157 kg.-cals., for the methylene group in paraffin hydrocarbons[6] and there can no longer be any doubt that Ruzicka's large-ring compounds are strain-free and multiplanar. Muscone, which occurs naturally in musk, was shown by Ruzicka to be β-methyl*cyclo*pentadecanone. Its racemic modification has now been synthesised independently by K. Ziegler and K. Weber [7] and by L. Ruzicka and M. Stoll.[8] The physical properties of compounds containing large carbon rings up to C_{33} have been revised.[8a]

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[50] P. Karrer and U. Solmssen, *Helv. Chim. Acta*, 1935, **18**, 1306.

[1] For general reviews, see (*a*) W. Hückel, *Fortschr. Chem. Physik*, 1927, **19**, Heft 4, 1, and " Grundlagen der Org. Chem.," I, 56 (1934); (*b*) W. H. Mills, *Inst. int. Chim. Solvay, Conseil Chim.*, 1931, **4**, 1; and Thorpe's " Dictionary of Applied Chemistry," II, 433 (1935).

[2] Attention must also be drawn to the pioneer work of J. Böeseken and H. G. Derx (*Rec. trav. chim.*, 1920, **39**, 183; 1921, **40**, 529; 1922, **41**, 327, 338; *A.*, 1921, i, 663, 843; 1922, i, 651), which provided the first experimental evidence in favour of the Sachse–Mohr theory.

[3] *Ann. Reports*, 1926, **23**, 112; 1928, **25**, 111.

[4] *Helv. Chim. Acta*, 1933, **16**, 162; *A.*, 1933, 230.

[5] W. Hückel, A. Gercke, and A. Gross, *Ber.*, 1933, **66**, [*B*], 563; *A.*, 1933, 494.

[6] F. D. Rossini, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 21; *A.*, 1934, 1071. Cf. *Ann. Reports*, 1934, **31**, 43.

According to Sachse the *cyclo*hexane ring should exist in two multiplanar strainless forms, but on theoretical grounds it is to be expected that these will be very easily interconvertible.[1b] For general stereochemical purposes the single ring can be considered as planar, in accordance with a mass of chemical evidence. There is no satisfactory evidence for the existence of isomeric monocyclic derivatives of *cyclo*hexane corresponding to the two Sachse forms. One claim [9] for this has been disproved [10] and another [11] appears to be against the weight of the evidence.[12]

Dicyclic Compounds.

The investigation of dicyclic compounds has now reached a stage when a general review can profitably be made. The results from this field are in many ways more precise than those coming from the study of the simple rings. It has been found that the tetrahedral arrangement is maintained and that deviations from this lead to strain, an increase in energy content, and a fall in stability. We may draw attention to the fortunate circumstance by which the *cis*- and the *trans*-locking of alicyclic rings were experimentally established just before the sudden development of the chemistry of sterols and allied substances, in which the two types of locking play so important a part.

The purely tetrahedral theory of ring strain, modified by Sachse, Mohr, and Hückel from Baeyer's original conception, makes the following requirements in the field of *ortho*-dicyclic systems.[1a] (a) Two five-membered rings can be fused by *cis*-valencies to yield a strain-free rigid structure containing two inclined planar rings, whereas fusion by *trans*-valencies gives a rigid strained multiplanar structure in which the minimum strain is almost exactly equal to that of the *bicyclo*[1 : 2 : 2]heptane (camphor) system. (b) Two six-membered rings can be joined by either *cis*- or *trans*-valencies to yield strainless multiplanar structures, the *cis*-forms being mobile, the *trans*- comparatively rigid.[13] (c) A five-membered ring can be fused to a six-membered ring by *cis*-valencies to give a strainless structure in which the 5-ring is planar and the 6-ring of the *C*-type. *trans*-Linking of these rings yields a strained multiplanar structure in which the minimum strain is about half that given by the *trans*-linking of two five-membered rings.

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[7] *Annalen*, 1934, **512**, 164; *A.*, 1934, 1103. For Ziegler's elegant methods, see *Ann. Reports*, 1934, **31**, 161.

[8] *Helv. Chim. Acta*, 1934, **17**, 1308; *A.*, 1934, 1220.

[8a] L. Ruzicka, M. Hürbin, and M. Furter, *ibid.*, p. 78; *A.*, 1934, 285.

[9] M. Qudrat-i-Khuda, *Nature*, 1933, **132**, 210; *A.*, 1933, 952.

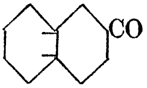
[10] A. N. Dey and R. P. Linstead, *J.*, 1935, 1063; *A.*, 1239.

[11] M. Qudrat-i-Khuda, *J. Indian Chem. Soc.*, 1931, **8**, 277; *A.*, 1931, 1055; *Nature*, 1935, **136**, 301; *A.*, 1236.

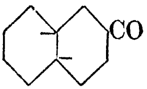
[12] S. Goldschmidt and G. Gräfinger, *Ber.*, 1935, **68**, [*B*], 279; *A.*, 489; R. D. Desai and R. F. Hunter, *Nature*, 1935, **136**, 608. Cf. *idem*, *ibid.*, **135**, 434; **136**, 953; *A.*, 618, 1495.

We shall consider first the preparation of substances of these types and secondly the manner in which their strain has been estimated.

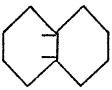
Decahydronaphthalenes (*Decalins*).[14]—W. Hückel[15] has conclusively established the existence of two series of decalin derivatives corresponding to the *cis*- and *trans*-linking of the two *cyclo*hexane rings. Two β-decalols had been known for some time. These were oxidised to two isomeric β-decalones (I), which were reduced by the Clemmensen or the Wolff method to the corresponding decalins (II). This showed that the cause of the isomerism lay in the arrangement of the ring carbon atoms and was not connected with the substituents. The *cis* (II*a*)- and *trans* (II*b*)-decalins can be separated by the fractionation of crude decalin, made by the reduction of naphthalene.



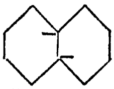
(I.) *cis*



(I.) *trans*



(II.) *cis*



(II.) *trans*

(*Plain hexagons in the formulæ in this section of the Report imply* cyclo*hexane, not benzene rings.*)

N. D. Zelinsky and M. B. Turova-Pollak[16] have shown that *cis*-decalin can be isomerised to the *trans*-form by aluminium chloride at room temperature. Reduction (catalytic or alkaline) of each of the two β-decalones yields a pair of isomeric β-decalols;[17] the two *cis*-forms melt at 105° and 18°; the two *trans*- at 75° and 53°. The purification of these has recently been improved by W. Hückel and K. Kumetat.[18] Reduction of the two β-decaloneoximes yields the corresponding four amines.[17] These compounds are of the type (III, $X = OH$ or NH_2).

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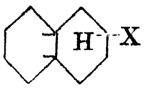
[13] The various decalins produced by fusing *C*- and *Z*-forms of the *cyclo*hexane ring can all be resolved into one *cis*- and one *trans*-form (W. A. Wightman, *J.*, 1925, **127,** 1421; *A.*, 1925, i, 894; cf. P. C. Henriquez, *Proc. K. Akad. Wetensch. Amsterdam,* 1934, **37,** 532; *A.*, 1935, 15, for a mathematical treatment).

[14] Continued from *Ann. Reports,* 1924, **21,** 92.

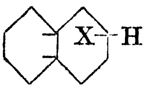
[15] *Annalen,* 1925, **441,** 1; *Ber.*, 1925, **58,** 1449; *A.*, 1925, i, 258, 1254.

[16] *Ber.*, 1929, **62,** 1658; 1932, **65,** 1299; cf. *ibid.*, 1925, **58,** 1292; *A.*, 1929, 921; 1932, 1122; 1925, i, 1053.

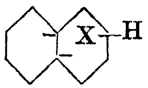
[17] W. Hückel, R. Mentzel, E. Brinkmann, and E. Kamenz, *Annalen,* 1927, **451,** 109; *A.*, 1927, 238.



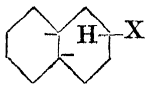
(IIIa.)



(IIIb.)

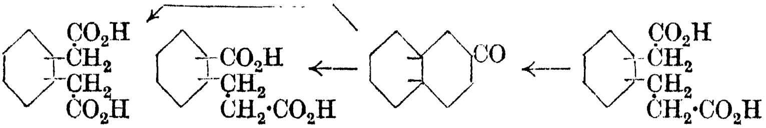


(IIIc.)



(IIId.)

The structure of the β-decalones was confirmed by their oxidation, which gave a mixture of *cyclo*hexane-1-carboxylic-2-propionic acids and *cyclo*hexane-1 : 2-diacetic acids (shown in *cis*-forms, IV and V), and also by the synthesis of *cis*-β-decalone from *cis*-*cyclo*hexane-1-acetic-2-propionic acid (VI).[15] This was originally prepared from 2-hydroxy-3-naphthoic acid and has recently been synthesised from *cyclo*hexanone.[19] *cyclo*Hexane-1 : 2-diacetic acid also has been synthesised recently.[19a]



(V.) (IV.) (VI.)

The isolation of the corresponding compounds with substituents on the α-carbon atom has proved more difficult, owing to the ease with which *cis*-α-decalone isomerises into the *trans*-compound. A paper by W. Hückel, R. Danneel, A. Gross, and H. Naab [20] has extended and revised earlier work.[15] Hydrogenation of α-naphthol over nickel yields two *trans*-α-decalols (m. p.'s 63° and 49°), which give the same *trans*-α-decalone (m. p. 33°) on oxidation. Reduction of either of the α-tetralols (*ac*- or *ar*-) over platinum yields a *cis*-α-decalol (m. p. 93°), which gives *cis*-α-decalone (m. p. 2°) on careful oxidation. This passes over readily and practically irreversibly into *trans*-α-decalone (m. p. 33°). The second *cis*-α-decalol (m. p. 55°) can only be obtained by treating the corresponding *cis*-α-decalylamine with nitrous acid. All four theoretically possible α-decalylamines [m. p.'s 8°, − 2° (*cis*) and − 1°, − 18° (*trans*)] have been prepared and characterised.

cis- and *trans*-α-Decalone (VII) on mild oxidation yield respectively the *cis*- and the *trans*-form of *cyclo*hexane-1-carboxylic-2-propionic acid (VIII), but treatment with permanganate at 100° leads to the complete ring fission of both ketones with the formation of δ-ketosebacic acid (IX), reducible to sebacic acid.[15] The esters of both *cis-* and *trans-cyclo*hexane-1-carboxylic-2-butyric acid when submitted to the Dieckmann reaction, give *trans*-α-decalone-β-carboxylic ester (X), which yields *trans*-α-decalone on ketonic fission.

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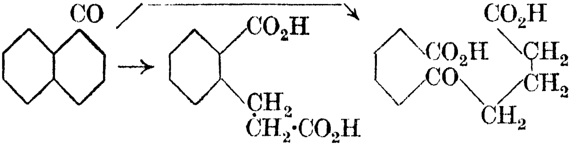
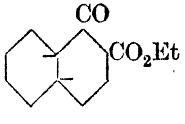
[18] *Ber.*, 1934, **67**, [*B*], 1890; *A.*, 1935, 80.

[19] J. W. Barrett, A. H. Cook, and R. P. Linstead, *J.*, 1935, 1065; *A.*, 1239.

[19a] C. K. Chuang and C. M. Ma, *Ber.*, 1935, **68**, [*B*], 871: *A.*, 859.

[20] *Annalen*, 1933, **502**, 99; *A.*, 1933, 603.

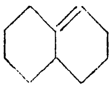




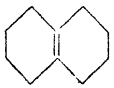
(VII.) *cis-* and *trans-* (VIII.) *cis-* and *trans-* (IX.) (X.)

The configuration of these compounds was deduced from that of the acids which they yield on oxidation (which was known with probability but not certainty) and from the physical properties of the dicyclic hydrocarbons and ketones. The Auwers–Skita rule is obeyed, the molecular refractivity of the *trans*-compounds being about 0·35 unit above that of their *cis*-isomerides, which is approximately normal.

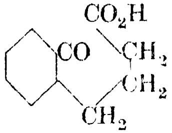
The absolute proof of the configuration follows from the optical resolution of *trans-cyclo*hexane-1 : 2-diacetic acid—derived from *trans*-β-decalol—which has been effected in two laboratories,[21, 22] and from W. Hückel and H. Friedrich's study [23] of the reduction of the β-hydrindanones (see below).



(XI.)



(XII.)



(XIII.)

Hückel and his collaborators [24] have prepared a number of octalins, of which the $\Delta^{1:9}$- and the $\Delta^{9:10}$- form are of particular interest. $\Delta^{1:9}$-Octalin (XI) is obtained by the pyrolysis of the methyl xanthates of *cis-* and *trans*-α-decalols or by the decomposition of their *p*-toluenesulphonates with alcoholic soda; $\Delta^{9:10}$-octalin (XII), by isomerising the $\Delta^{1:9}$-isomeride with *p*-toluenesulphonic acid and by other methods.[25] Ozonisation of $\Delta^{1:9}$-octalin yields γ-2-keto*cyclo*hexylbutyric acid (XIII), which with

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[21] W. Hückel, M. Sachs, J. Yantschulewitsch, and F. Nerdel, *Annalen*, 1935, **518**, 155; *A.*, 971, following preliminary work (ref. 23).

[22] J. W. Barrett and R. P. Linstead, *J.*, 1935, 1069; *A.*, 1239.

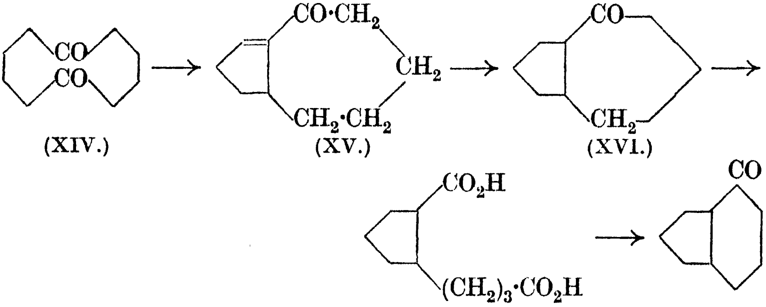
[23] *Annalen*, 1926, **451**, 132; *A.*, 1927, 238.

[24] W. Hückel, R. Danneel, A. Schwartz, and A. Gercke, *ibid.*, 1929, **474**, 121; **477**, 99; *A.*, 1930, 76, 206; W. Hückel and H. Naab, *ibid.*, 1933, **502**, 136; *A.*, 1933, 704.

[25] Cf. *Ann. Reports*, 1930, **27**, 159.

permanganate gives δ-ketosebacic acid (IX). This proves that the double bond is at the bridge-head, contrary to Bredt's rule. Tetrahedral models show, however, that $\Delta^{1:9}$-octalin is free from strain, and this agrees with its heat of combustion, which is about the same as that of $\Delta^{2:3}$-octalin.[24] Bredt's rule must therefore be applied with discrimination. If two rings can be locked in the *ortho*-position by *trans*-valencies to yield a stable system, an unsaturated derivative with the double bond attached to the bridge-head will be equally stable. The rule breaks down for rings above the 5-membered, but would be obeyed in the *bicyclo*[0 : 3 : 3]-octane and probably in the hydrindane series.

The *cyclo*decanedione (XIV) obtained by ozonising $\Delta^{9:10}$-octalin[25] undergoes an internal condensation in the presence of alkali to yield an unsaturated monoketone (XV) in which 5- and 7-membered rings are fused together and the double bond can adjoin the bridge-head without strain.[26] The mixture of *cis*- and *trans*-*cyclo*pentano-*cyclo*heptanones (XVI) obtained by its reduction has been degraded to hydrindan-4-one (XVII):



(XIV.) (XV.) (XVI.) (XVII.)

Hydrindanes.[27]—W. Hückel and H. Friedrich[23] showed that *cis*- and *trans*-*cyclo*hexane-1 : 2-diacetic acids were cyclised to two different β-hydrindanones (XVIII*a* and *b*), oxidation of which yielded the corresponding *cis*- and *trans*-*cyclo*hexane-1-carboxylic-2-acetic acids, which had already been shown to be interconvertible through their anhydrides.[28] As was pointed out by Hückel, the

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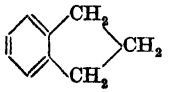
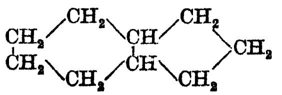
[26] W. Hückel and L. Schnitzspahn, *Annalen*, 1933, **505**, 274; *A.*, 1933, 1163.

[27] A simplified nomenclature is used:



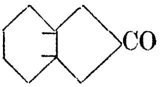
(hydrindene = indane)



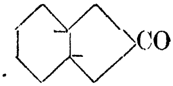
(hexahydro-hydrindene = hydrindane)

[28] A. Windaus, W. Hückel, and G. Reverey, *Ber.*, 1923, **56**, 91; *A.*, 1923, i, 220.

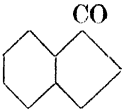
trans-ketone on reduction should yield one racemic *trans*-hydrindanol whereas the *cis*-ketone should give two *ms*-alcohols. These were actually isolated.[23, 21] The corresponding two *cis*- and one *trans*-forms of β-hydrindanylamine have also been prepared.[21]



(XVIII*a*.)



(XVIII*b*.)



(XIX.)

Complete reduction of the *cis*- and the *trans*-ketone yielded the *cis*- and the *trans*-form, respectively, of hydrindane, mixtures of which had already been obtained by the hydrogenation of indene. *trans*-β-Hydrindanone has been obtained in optically active forms[21, 22] and the *l*-ketone, $[\alpha]_{5461}^{17\cdot5^{\circ}}$ − 337°, has been reduced to *l*-*trans*-hydrindane, $[\alpha]_{5461}^{19^{\circ}}$ − 11°.[22]

Earlier work[28] had shown that both the *cis*- and the *trans*-form of *cyclo*hexane-1-carboxylic-2-propionic acid (VIII) yielded the same α-hydrindanone (XIX) on cyclisation. A similar result was achieved by cyclising the esters of these acids by the Dieckmann method and hydrolysing the product. The ketone obtained appears to be a mixture in which the *cis*-form greatly predominates. It yields a mixture of oximes in the ratio 10 *cis*- : 1 *trans*-. The position of equilibrium between the two α-ketones has not, however, been rigidly established.

A number of hydrindanones substituted in the *cyclo*hexane ring have been prepared,[26, 29, 30] of which the most interesting from the stereochemical point of view is hydrindan-4-one (XVII). The *cis*- and the *trans*-form of this should be interconvertible. Here again the weight of the evidence is that the *cis*- is the more stable modification.

bicyclo(0 : 3 : 3)-*Octanes*.—The group of *ortho*-fused cyclic compounds has been completed by the preparation of substances in which two *cyclo*pentane rings are joined by *cis*- and by *trans*-valencies. *cyclo*Pentane-1 : 2-diacetic acid has been synthesised in both *cis*- and *trans*-forms (XX*a* and *b*) from *cyclo*pentanone-carboxylic ester.[31, 32, 33] The two acids are conveniently separated by fractional ketonisation: the *cis*-acid yields the strain-free *cis*-β-*bicyclo*octanone (XXI*a*) when distilled with baryta at 290°,

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[29] A. H. Cook and R. P. Linstead, *J.*, 1934, 946; *A.*, 1934, 1002.

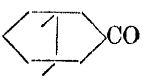
[30] W. Hückel and E. Goth, *Ber.*, 1934, **67**, [*B*], 2104; W. Hückel and R. Schlüter, *ibid.*, p. 2107; *A.*, 1935, 208, 215.

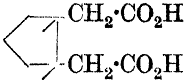
[31] R. P. Linstead and E. M. Meade, *J.*, 1934, 935; *A.*, 1934, 1002.

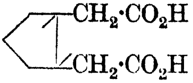
[32] W. Hückel, E. Goth, and G. Demmler, *Ber.*, 1934, **67**, [*B*], 2102; *A.*, 1935, 211.

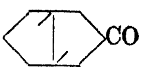
[33] J. W. Barrett and R. P. Linstead, *J.*, 1935, 436; *A.*, 750.

whereas the *trans*-acid only yields the corresponding strained ketone (XXI*b*) at 340°.[33]


(XXI*a*.)

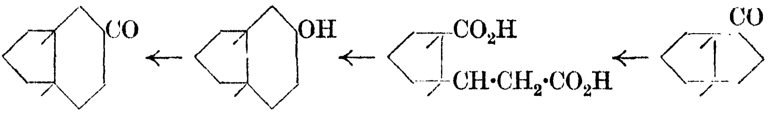

(XX*a*.)


(XX*b*.)


(XXI*b*.)

The structure of these ketones was proved by their oxidation to *cis*- and *trans*-*cyclo*pentane-1-carboxylic-2-acetic acids, which were independently synthesised.[34] The ketones and the two hydrocarbons obtained by their reduction show differences in physical properties, comparable with those found in the decalin and hydrindane series.[29, 33]

Catalytic reduction of 5-hydroxyindane in acetic acid yielded 5-hydrindanol (XXII)—essentially *cis*—which on oxidation with chromic acid gave the corresponding ketone (XXIII) and with nitric acid *cis*-*cyclo*pentane-1-carboxylic-2-acetic acid (XXIV).[29, 35] It has been shown by A. H. Cook and R. P. Linstead that both this acid and its *trans*-isomeride yield the same α-*bicyclo*octanone on cyclisation either directly or through the esters by the Dieckmann method. In contradistinction to the decalones, the stable form obtained in this way is the *cis*-isomeride (XXV). *cis*-5-Hydrindanone (XXIII) has been synthesised from *cyclo*pentanonecarboxylic ester[29] and the whole series of reactions provides a proof by degradation of the presence of the 5-membered ring in indene.


(XXIII.) (XXII.) (XXIV.) (XXV.)

Two other syntheses of derivatives of *cis*-*bicyclo*octane have been recorded.[36]

The configurations given above have been rigidly proved by the resolution of *trans*-*cyclo*pentane-1 : 2-diacetic acid[22] (XX*b*). The *l*-form of this acid was cyclised to *d*-*trans*-β-*bicyclo*octanone (XXI*b*). The optical activity of this ketone, $[\alpha]^{18^\circ}_{5461}$ + 437°, shows that its constituent rings are multiplanar. The *d*-ketone on reduction yielded inactive *trans*-*bicyclo*octane in which the bridge carbon atoms are no longer asymmetric.[22] This provides an interesting contrast to the reduction of active *trans*-β-hydrindanone (p. 311).

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[34] A. H. Cook and R. P. Linstead, *J.*, 1934, 956; *A.*, 1934, 1003.

[35] W. Hückel and E. Goth, *Ber.*, 1934, **67**, [*B*], 2104; *A.*, 1935, 208.

[36] L. Ruzicka, A. Borges de Almeida, and A. Brack, *Helv. Chim. Acta*, 1934, **17**, 183; *A.*, 1934, 297; J. C. Bardhan and S. K. Banerji, *J.*, 1935, 474; *A.*, 748.

Turning to the estimation of the strain in these compounds, we need consider only two methods. Neither of these is completely satisfactory from a theoretical point of view, but they are the best available. The first is based on the assumption that a strained substance of suitable structure will tend to pass into a strain-free or less strained isomeride; the extent of the change will provide an approximate experimental indication of the strain. In this connection it is instructive to compare the carbocyclic substances described above with heterocyclic compounds of allied structure. Suitable substances are the anhydrides of 1 : 2-cyclic acids, a number of which have been obtained in *cis*- and *trans*-modifications.[37] The ring oxygen atom in these compounds is presumed to display tetrahedral symmetry; the length of the C–O bonds is less than that of the C–C, but not sufficiently to vitiate the comparison. The table summarises the results.

System.	Constituent rings.*	Strain-free forms.	Equilibrium.	Reference.
α-Decalone	6—6	*cis* and *trans*	*trans*	15
*cyclo*Hexane-1-carboxylic-2-acetic anhydride	6—6	,,	75% *trans*	28
α-Hydrindanone	5—6	*cis*	Mainly *cis*	21, 23
4-Hydrindanone	6—5	,,	,,	30
*cyclo*Hexane-1 : 2-dicarboxylic anhydride	5—6	,,	*cis*	38
*cyclo*Pentane-1-carboxylic-2-acetic anhydride	6—5	,,	86% *cis*	34
α-*bicyclo*Octanone	5—5	,,	*cis*	29
*cyclo*Pentane-1 : 2-dicarboxylic anhydride	5—5	,,	,,	39

* The ring containing the α-group (CO) which promotes the interchange is written first.

Apart from the low stability of the *cis*-forms of the 6—6 systems, commented on later, the results agree with theory.

The most rigid evidence for strain available at present comes from the measurement of heats of combustion. It is assumed that in a comparison of isomeric substances of similar physical characteristics a higher heat of combustion will correspond with a greater content of energy, arising from the deviation of the carbon valencies from the normal tetrahedral angle. The heats of combustion of the highly purified dicyclic carbon compounds already mentioned have been measured by W. A. Roth and G. Becker with the results summarised below. The heats of combustion are expressed in the usual form as kg.-cals./mol. of liquid at constant volume; the more exact comparison in which the values are corrected to the vapour state gives no significant change in the differences (Δ) in column 4.

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[37] For other *cis*- and *trans*-fused-ring compounds containing a heterocyclic ring, see *Ann. Reports*, 1928, **25**, 183; 1929. **26**, 164; 1930, **27**, 161.

[38] A. v. Baeyer, *Annalen*, 1890, **258**, 218; *A.*, 1890, 1275.

[39] The *trans*-anhydride yields the *cis*-anhydride on heating (W. H. Perkin *et al.*, *J.*, 1894, **65**, 985; 1914, **105**, 2643). The *trans*-anhydride is polymeric (J. Bredt, H. Thouet, and J. Schmitz, *Annalen*, 1924, **437**, 1; *A.*, 1924, i, 643).

Substance.	*cis*-Form.	*trans*-Form.	Δ (*trans*- – *cis*-).	Reference.
Decalin	1499·9	1495·2	– 4·7	40
β-Decalone	1402·3	1400·1	– 2·2	40
Hydrindane	1347·5	1345·7	– 1·8	21
β-Hydrindanone	1245	1243·9	– 1·1	21, 23
*bicyclo*Octane	1197·7	1203·8	+ 6·1	41
β-*bicyclo*Octanone	1094·1	1100·9	+ 6·8	33

The difference between the heats of combustion of the *cis*- and the *trans*-*bicyclo*octane derivatives provides an experimental demonstration of the reality of strain. This is particularly acceptable, as the much-quoted figures for the heats of combustion of the *cyclo*propane and *cyclo*butane rings rest on uncertain experimental foundation.[42] The values for the *cis*-form of the hydrindane ring are a little higher than those for the *trans*- (the difference was larger in earlier experiments), which is the opposite of that expected on theoretical grounds. It appears that a second factor operates in these dicyclic substances, tending to make the *cis*-forms less stable than expected from the simple tetrahedral theory. This factor shows itself in the decalin series in the heats of combustion and also in the tendency of the *cis*- to pass into the *trans*-form. This appears to be a manifestation of a general phenomenon: when no question of strain arises, *cis*-compounds usually have a heat of combustion higher than that of their *trans*-isomerides by about 2 kg.-cals., although exceptions are known.[43] Theoretical explanations have been advanced.[1]

Thermochemical evidence of strain has also come from K. Alder and G. Stein's study of polymeric cyclic hydrocarbons.[44] Tetrahydro-α-di*cyclo*pentadiene [45] (XXVI) contains the norcamphor (*bicyclo*[1 : 2 : 2]-heptane) ring system (XXVII) fused by *cis*-valencies

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[40] W. A. Roth and R. Lassé, *Annalen*, 1925, **441**, 48; *A.*, 1925, ii, 275.

[41] J. W. Barrett and R. P. Linstead, unpublished; measurements by G. Becker.

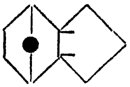
[42] M. S. Kharasch, *J. Res. Nat. Bur. Stand.*, 1929, **2**, 359; *A.*, 1929, 511; F. Richter, *Chem. Reviews*, 1932, **10**, 385.

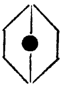
[43] P. A. Verkade, J. Coops, *et al.*, *Annalen*, 1930, **477**, 279; *A.*, 1930, 337; A. Wassermann, *Z. physikal. Chem.*, 1930, [*A*], **146**, 418; **151**, 113; *A.*, 1930, 524; 1931, 42.

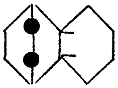
[44] *Ber.*, 1934, **67**, [*B*], 613; *A.*, 1934, 641.

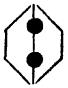
[45] For the preparation of these and similar substances, see K. Alder and G. Stein, *Annalen*, 1932, **496**, 197, 204; *A.*, 1932, 938; *ibid.*, 1933, **501**, 247; **504**, 205, 216; *A.*, 1933, 508, 942.

to a strain-free *cyclo*pentane ring. The molecule should have a strain practically identical with that of *trans-bicyclo*(0 : 3 : 3)-octane. Tetrahydrodi*cyclo*hexadiene [45] has a similar general arrangement, but contains a *cyclo*hexane ring fused in the *cis*-position to the *bicyclo*(2 : 2 : 2)-octane structure (XXIX) and is strainless.


(XXVI.)


(XXVII.)


(XXVIII.)


(XXIX.)

The difference between the heats of combustion of (XXVI) and (XXVIII), strain being neglected, should be twice the value for CH_2, or about 314 kg.-cals. The experimental difference [46] is 307 kg.-cals. If the figures are corrected to the vapour state, tetrahydrodi*cyclo*pentadiene has a heat of combustion higher than that calculated from the value for (XXIX) by 6·3 kg.-cals. A similar comparison [44, 46, 47] between the strained norcamphor and the strain-free 2 : 5-*endo*ethylene*cyclo*hexanone [ketones corresponding to (XXVII) and (XXIX)] gives a value for the CH_2 group of 151·7 kg.-cals., *i.e.*, about 5·3 kg.-cals. less than normal. The correction to the vapour state is possible owing to J. Pirsch's determination of the molecular freezing-point depression constants.[47] Direct comparison between camphor itself and the isomeric β-decalones (vapour) shows that the former has a higher heat of combustion by 6—8 kg.-cals. (according to which decalone is taken), but here there may be some complication due to the methyl groups of camphor.

To summarise: the tetrahedral theory predicts that the *trans-bicyclo*[0 : 3 : 3]-octane and the *bicyclo*[1 : 2 : 2]-heptane * system will both be strained and by the same amount. The heats of combustion (vapour) of substances containing these systems have an exaltation over their strain-free isomerides, or over values calculated from strain-free substances of similar structure, of about 6 kg.-cals. The concordance of the experimental exaltations mentioned above from five different comparisons may be partly fortuitous, but is very striking. Another satisfactory feature is that the heats of combustion of *cis*-β-*bicyclo*[0 : 3 : 3]-octanone and *bicyclo*[2 : 2 : 2]-octanone,[44] which are isomerides containing quite different strain-free systems, are almost identical, 1105·4 and 1104·9.[33, 47]

Attention may be drawn to G. Komppa's synthesis [48] of *bicyclo*-

[46] G. Becker and W. A. Roth, *Ber.*, 1934, **67**, [*B*], 627; *A.*, 1934, 734.

[47] *Ibid.*, p. 1303; *A.*, 1934, 951.

[48] *Ber.*, 1935, **68**, [*B*], 1266; *A.*, 1123.

* The *cis*-form; the *trans*-form appears incapable of existence.

[2 : 2 : 2]-octanone (2 : 5-*endo*ethylene*cyclo*hexanone) and of *bicyclo*[2 : 2 : 2]-octane (XXIX). The products were identical with those already prepared by the diene method,[49] and the new synthesis confirms the structure. Compounds containing this very symmetrical arrangement of carbon atoms, or the similarly bridged *bicyclo*[1 : 2 : 2]-heptane system (XXVII), are characterised by high melting points, exceptional volatility,[48] and very high molecular freezing-point depressions.[47, 50] *bicyclo*[2 : 2 : 2]-Octanes can be dehydrogenated to aromatic hydrocarbons in the usual way, the bridge being broken.[51] K. Alder, G. Stein, and their collaborators have extended their stereochemical investigation of the polymerisation of cyclic diolefins [45] to the reaction of maleic anhydride with these hydrocarbons.[52] This work has reopened the old problem of the configuration of borneol and *iso*borneol, for which the original memoir should be consulted.

Sterols and Sex Hormones.

There has been considerable activity in the course of the last few years in the preparation of the aromatic dehydrogenation products of the sterols and similar products. During the past year this has spread, particularly in this country, to attempts at the synthesis of the actual reduced ring systems themselves. This work, although of exceptional interest, has not yet reached a stage suitable for a general report.

Research has again been active among the natural products themselves, particularly the sterols and sex hormones, but as the group has been fully reviewed in preceding years, a report of this field is postponed. R. P. L.

6. TERPENES.*

(Continued from *Ann. Reports*, 1932, **29**, 147.)

General.

Recent work is emphasising the need for caution in the interpretation of the results of ozonisation of substances containing one of the common terminal groups (I) and (II).

$\mathrm{CMe_2{:}}$ (I.) $\mathrm{CH_2{:}CMe{\cdot}}$ (II.) $\mathrm{CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CO_2H}$ (III.)

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[49] O. Diels and K. Alder, *Annalen*, 1930, **478**, 137; *A.*, 1930, 472; K. Alder and G. Stein, *ibid.*, 1934, **514**, 13; *A.*, 1934, 211.

[50] J. Pirsch, *Ber.*, 1934, **67**, [*B*], 101; *A.*, 1934, 285.

[51] B. A. Kasansky and A. F. Plate, *Ber.*, 1935, **68**, [*B*], 1259; *A.*, 1112.

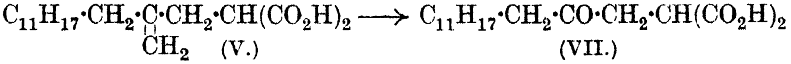
[52] *Annalen*, 1934, **514**, 1, 197, 211; 1935, **515**, 165, 185; *A.*, 1935, 211, 341, 219, 349, 350.

* For a recent general account, see J. L. Simonsen, *J.*, 1935, 781.

The ozonisation of many liquid terpene derivatives of this type, such as citronellol, gives both acetone and formaldehyde, derived from (I) and (II) respectively.[1] This has usually been taken as implying that the natural products are mixtures of the two types. The oxidation of dehydrogeranic acid, which is a crystalline solid, also gives anomalous results. R. S. Cahn, A. R. Penfold, and J. L. Simonsen [2] found that the acid from natural sources (m. p. 186°) yielded both acetone and formic acid on permanganate oxidation. R. Kuhn and H. Roth, in the course of a general investigation,[3] observed that this acid and its synthetic stereoisomeride (m. p. 137°) gave a comparatively poor yield (*ca.* 60%) of acetone on ozonisation, followed by treatment with permanganate. Nevertheless the absorption spectra of these acids indicate that both are practically pure (III). In view of these results Kuhn considers it possible that the usual preparations of citronellol, which give a maximum of 80% of acetone on ozonisation, are pure *iso*propylidene compounds, and do not contain 20% of rhodinol, as previously thought.

Another curious anomaly is that recently observed by A. E. Bradfield, A. R. Penfold, and J. L. Simonsen [4] in the oxidation of α-santalylmalonic acid (IV or V; for full formula, see p. 328). This substance yields tri*cyclo*ekasantalic acid (VI) on ozonisation, but the keto-acid (VII) on oxidation with alkaline permanganate :

$$\underset{\text{(VI.)}}{C_{11}H_{17}\cdot CO_2H} \longleftarrow \underset{\text{(IV.)}}{C_{11}H_{17}\cdot CH{:}CMe\cdot CH_2\cdot CH(CO_2H)_2}$$



$$\underset{\text{(V.)}}{C_{11}H_{17}\cdot CH_2\cdot \underset{CH_2}{\overset{\parallel}{C}}\cdot CH_2\cdot CH(CO_2H)_2} \longrightarrow \underset{\text{(VII.)}}{C_{11}H_{17}\cdot CH_2\cdot CO\cdot CH_2\cdot CH(CO_2H)_2}$$

These results point to formulæ (IV) and (V) respectively for the parent acid, which is, however, a well-defined crystalline solid. It is suggested that the double bond is mobile under the conditions of oxidation or even merely on solution, which recalls A. Verley's views on the ozonisation of the acyclic terpenes.[5] Further experimental work in the field is necessary before a final explanation can be reached. G. R. Clemo and J. M. MacDonald's results [6] emphasise that only quantitative estimation of formaldehyde can be taken as proving the presence of a vinyl group in terpenes and similar compounds.

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[1] *E.g.*, V. Grignard and J. Dœuvre, *Compt. rend.*, 1928, **187**, 270, 330; J. Dœuvre, *Bull. Soc. chim.*, 1929, [iv], **45**, 352; *A.*, 1928, 1113; 1929, 542.

[2] *J.*, 1931, 3134; *A.*, 1932, 144.

[3] *Ber.*, 1932, **65**, [*B*], 12; *A.*, 1932, 1111.

[4] *J.*, 1935, 311; *A.*, 755.

[5] *E.g.*, *Bull. Soc. chim.*, 1928, [iv], **43**, 854; *A.*, 1928, 1139.

[6] *J.*, 1935, 1294; *A.*, 1390.

Percamphoric acid has been introduced [7] as a substitute for perbenzoic acid in the estimation of double bonds in unsaturated compounds. It appears to be more stable than the older reagent, but cannot be used when the double bond is in the αβ-position with respect to carboxyl, carbonyl, or a similar group.

Selenium dioxide, originally introduced as an oxidising agent by H. L. Riley,[8] has been applied to a number of oxidations in the terpene field. The following conversions have been recorded: α-pinene ⟶ verbenone;[9, 10] α-pinene ⟶ myrtenol and myrtenal;[11] nopinene ⟶ pinocarvone;[10] camphor ⟶ camphorquinone;[12] borneol ⟶ camphorquinone;[13] menthones ⟶ menthenones;[14] α-phellandrene ⟶ cumaldehyde;[14] piperitone ⟶ thymol.[14]

Monoterpene Group.

Menthols.—Of the substances related to the terpenes, the menthols and menthones are among those most fully studied from the stereochemical side. The thorough investigation of these substances by J. Read and his co-workers has now led to the isolation of all the four possible series of menthols and menthylamines. Extending the earlier studies of Beckmann, Pickard and others, Read examined the reduction of piperitones (VIII),* which yielded mixtures of menthone and *iso*menthone (IX*a* and *b*), related as *cis-trans*-isomerides.[15] Corresponding to each of these ketones there are two resolvable alcohols (type X), menthol and neomenthol from menthone, *iso*menthol and neo*iso*menthol from *iso*menthone. The two series can be separated (i) by reduction of the ketones to the alcohols, best by Ponndorf's method,[16, 17] and purification through the hydrogen phthalates or by competitive esterification; or (ii) by reduction of the oximes of the ketones to menthylamines, separation of these as salts, and conversion into menthols. The pure alcohols can be oxidised back to the ketones without change of configuration.

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[7] N. A. Milas and A. McAlevy; N. A. Milas and I. S. Cliff, *J. Amer. Chem. Soc.*, 1933, **55**, 349, 352; *A.*, 1933, 279.

[8] For recent general work, see *J.*, 1935, 901; *A.*, 1231.

[9] E. Schwenk and E. Bergwardt, *Ber.*, 1932, **65**, [*B*], 1601.

[10] G. Dupont, J. Allard, and R. Dulon, *Bull. Soc. chim.*, 1933, [iv], **53**, 599; *A.*, 1933, 1166.

[11] G. Dupont and W. Zacharewicz, *ibid.*, 1935, [v], **2**, 533; *A.*, 624.

[12] W. C. Evans, J. M. Ridgion, and J. L. Simonsen, *J.*, 1934, 137; *A.*, 1934, 299.

[13] J. Allard, *Bull. Inst. Pin.*, 1934, 127; *A.*, 1934, 1106.

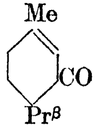
[14] E. Bergwardt and E. Schwenk, *J. Amer. Chem. Soc.*, 1934, **56**, 1185; *A.*, 1934, 777; J. Tabuteau, *Compt. rend.*, 1935, **200**, 244; *A.*, 624.

[15] For a summary of the earlier work, see J. L. Simonsen, "Terpenes," I, 201 (1931); J. Read, *Chem. Reviews*, 1930, **7**, 1.

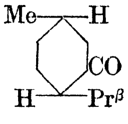
[16] W. Ponndorf, *Z. angew. Chem.*, 1926, **39**, 138; *A.*, 1926, 520.

[17] O. Zeitschel and H. Schmidt, *Ber.*, 1926, **59**, 2298; *A.*, 1926, 1250; *J. pr. Chem.*, 1932, **133**, 365.

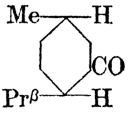
* *dl*-Piperitone has recently been synthesised by J. Walker (*J.*, 1935, 1585).



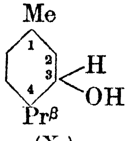
(VIII.)



(IX*a*.)



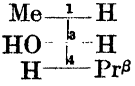
(IX*b*.)

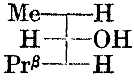


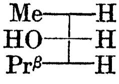
(X.)

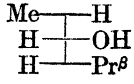
In the earlier work both menthones and three of the menthols (menthol itself, *iso*menthol, and neomenthol) were obtained in both active and racemic forms in a state of purity. *dl*- and *d*-Neo*iso*menthol have now [18, 19] been obtained pure from *dl*- and *l*-*iso*menthone respectively by Ponndorf reduction and separation of the alcohols by competitive esterification. They have also been isolated from the mixture of alcohols obtained by the hydrogenation of *dl*- or *l*-piperitone by purification through the hydrogen phthalate and the compounds with phosphoric acid.[20] H. Schmidt and L. Schulz [21] also have described the preparation of a neo*iso*menthol by reduction of *d*-*iso*menthone, either catalytically or by means of aluminium ethoxide, which causes some inversion. Their specific rotation ($\alpha_D - 0° 20'$) differs slightly from that found by Read (below).

The configuration of these substances has been discussed by J. Read and W. J. Grubb.[22] Following up earlier experiments by G. Vavon and A. Couderc,[23] they examined the ease of reaction between the menthols and various nitrobenzoyl chlorides. The reaction velocities with *p*-nitrobenzoyl chloride on a comparative basis are: menthols, 16·5; *iso*menthols, 12·3; neo*iso*menthols, 3·1; neomenthols, 1·0. If steric hindrance is the determining factor in these esterifications, the hydroxyl group must be *cis*- to *iso*propyl in the unreactive neomenthols. A survey of the evidence [22] has led to the following configurations, which correct earlier schemes: [24]









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[18] J. Read and W. J. Grubb, *J.*, 1934, 313; *A.*, 1934, 528.

[19] *Idem*, *J. Soc. Chem. Ind.*, 1934, **53**, 52T; *A.*, 1934, 413.

[20] Cf. J. W. Blagden and W. E. Huggett, *J.*, 1934, 317; *A.*, 1934, 528.

[21] *Ber. Schimmel*, 1934, 97; *A.*, 1935, 349.

[22] *J.*, 1934, 1779; *A.*, 1935, 88.

[23] *Compt. rend.*, 1924, **179**, 405; *A.*, 1924, i, 1210.

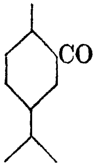
[24] J. Read *et al.*, *J.*, 1927, 2170; 1930, 2761; *A.*, 1927, 1080; 1931, 228.

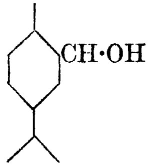
The alcohols derived from menthone contain the alkyl groups in the *trans*-position. The physical constants of these substances and the specific rotations of the associated menthylamines,[18, 22] tabulated below, show interesting relationships :

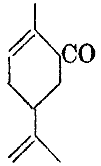
	Menthols.	Neo-menthols.	*iso*-Menthols.	Neo*iso*menthols.
M. p. of *dl*-	35° to 38°	53°	53·5°	14°
M. p. of *d*- or *l*- ...	42 to 43	— 22	82·5	— 8
$[\alpha]_D$ of menthols ...	— 49·6	+ 20·7	+ 25·9	+ 2·2 (in alcohol)
$[\alpha]_D$ of menthylamines...............	— 44·5	+ 15·1	+ 29·0	+ 2·3 (homogeneous)

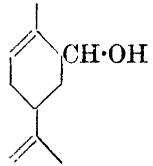
These configurations differ from those assigned by O. Zeitschel and H. Schmidt,[17] mainly on the basis of the greater ease of dehydration of menthols of the neo-series to Δ^3-menthene. Read regards this as a *trans*-elimination of water. His views are supported [25] by the fact that the monobenzoate of *trans-cyclo*hexane-1 : 2-diol (the configuration of which follows absolutely from its optical resolution) [26] reacts more readily with nitrobenzoyl chlorides than does the corresponding derivative of the *cis*-diol. It is, however, difficult to arrive at a final solution of such problems by chemical methods.

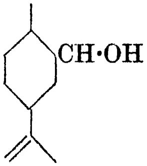
A similar study of the carvomenthone series has now been commenced by J. Read and R. G. Johnston.[27] The aims and methods are essentially the same, and the full study of the carvomenthones (XI) and carvomenthols (XII) has involved an examination of the corresponding unsaturated compounds, the carvones (XIII), carveols (XIV), and dihydrocarveols (XV). The entry into the *iso*-series comes in this case from the reduction of natural *d*-carvone, which yields a mixture of *l*-carvomenthone and *l-iso*-carvomenthone. Both saturated ketones and three of the alcohols have been obtained optically pure and many erroneous data have been corrected.


(XI.)


(XII.)


(XIII.)


(XIV.)


(XV.)

Hydrogenation of unsaturated compounds has also been used by H. Schmidt and L. Schulz [21] in an investigation of the stereoisomerism of the pinocampheols and pinocamphones. In this case

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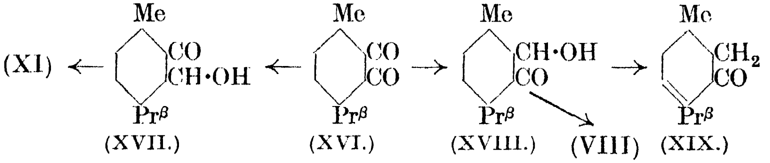
[25] N. A. B. Wilson and J. Read, *J.*, 1935, 1269; *A.*, 1493.

[26] H. G. Derx, *Rec. trav. chim.*, 1922, **41**, 312; *A.*, 1922, i, 651.

[27] *J.*, 1934, 226, 233; *A.*, 1934, 413, 414; *J.*, 1935, 1138; *A.*, 1245.

d- and *l*-pinocarveols yield *cis-d*- and *l*-pinocampheols. In all, two racemic and four active pinocampheols have been isolated, which on oxidation give the corresponding pinocamphones.

J. Walker and J. Read [28] have re-examined the catalytic hydrogenation of diosphenol (XVI), obtained by the oxidation of menthone, which G. Cusmano and R. Boccucci [29] had shown to yield 3-hydroxycarvomenthone (XVII) in the presence of platinum-black. This was converted into carvomenthone (XI). By reducing (XVI) with colloidal palladium, Walker and Read obtained the keto-alcohol (XVIII), convertible into Δ^4-menthen-3-one (XIX) and piperitone (VIII), both of the menthone series.



These changes show that diosphenol can act as a "turntable" between the menthone and the carvomenthone group ; this may be of biological significance.

Attention may be drawn to J. Clark and J. Read's attractive process [30] whereby a small amount of an active menthol can be used autocatalytically for the resolution of an indefinite amount of *dl*-menthol. A similar method has been used for the purification of crude *d*- and *l*-borneols. *l*-Mandelic acid also has been employed for the resolution of *dl*-menthol.[31]

Carenes.—Three gaps in the chemistry of the carene group have been filled by J. Owen and J. L. Simonsen. Homocaronic acid has been synthesised [32] in *cis*- and *trans*-forms, the *cis*-modification being identical with the acid obtained by the oxidation of *d*-Δ^3-carene. Synthetic *trans-dl*-caronic acid has been resolved [33] by means of the nor-ψ-ephedrines into the *d*- and the *l*-form, the latter of which is identical with the acid obtained by the oxidation of *d*-Δ^3- and Δ^4-carenes, and also by the oxidation of chrysanthemum mono- and di-carboxylic acids.[34] *cis-dl*-3-Carboxy-1 : 1-dimethyl*cyclo*propane-2-propionic acid had been synthesised by Owen and

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[28] *J.*, 1934, 238; *A.*, 1934, 414.

[29] *Gazzetta*, 1923, **53**, 649; *A.*, 1923, i, 1214.

[30] *J.*, 1934, 1773, 1775; *A.*, 89; cf. J. Read and W. J. Grubb, *J. Soc. Chem. Ind.*, 1932, **51**, 329T; *J.*, 1933, 167; *A.*, 1932, 1139; 1933, 397.

[31] A. McKenzie and (Miss) E. M. Luis, *J.*, 1934, 715; *A.*, 1934, 777.

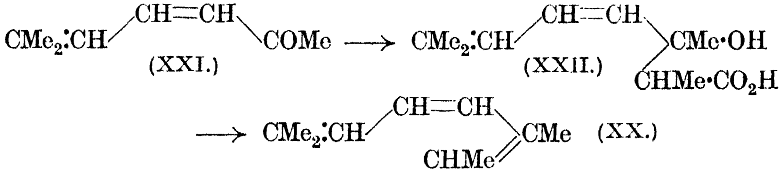
[32] *J.*, 1933, 1225; *A.*, 1933, 1160.

[33] J. Owen and J. L. Simonsen, *ibid.*, p. 1223; *A.*, 1933, 1160.

[34] H. Staudinger and L. Ruzicka, *Helv. Chim. Acta*, 1924, **7**, 201; *A.*, 1924, i, 510.

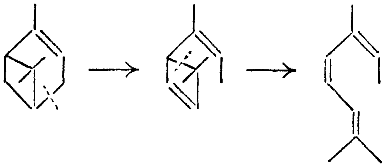
Simonsen.[35] They have now resolved the acid[33] and identified the *d*-form with one of the oxidation products of *d*-Δ^4-carene.

Pyrolysis of α-Pinene.—It has long been known that α-pinene is decomposed at high temperatures with the formation of dipentene, various aromatic hydrocarbons, and a diterpene. B. A. Arbusov[36, 37] has now found that α-pinene, passed over glass or various metallic surfaces, at about 350°, yields some 25% of an acyclic terpene. This is identical with *allo*ocimene (XX), a substance allied to myrcene and obtained by boiling the unstable natural terpene, ocimene. *allo*Ocimene has been synthesised[38] from methylheptadienone (XXI) by condensation with α-bromopropionic ester and zinc. The β-hydroxy-acid (XXII) obtained by the hydrolysis of the primary condensation product gave a good yield of *allo*ocimene on heating. This is an interesting example of the readiness with which unsaturated β-hydroxy-acids are decarboxylated. According to F. G. Fischer and K. Löwenberg[38] a β-lactone may act as an intermediate.



$$\mathrm{CMe_2{:}CH{\cdot}CH{=}CH{\cdot}COMe}\ \text{(XXI.)} \longrightarrow \mathrm{CMe_2{:}CH{\cdot}CH{=}CH{\cdot}CMe(OH){\cdot}CHMe{\cdot}CO_2H}\ \text{(XXII.)} \longrightarrow \mathrm{CMe_2{:}CH{\cdot}CH{=}CH{\cdot}CMe{:}CHMe}\ \text{(XX.)}$$

The identity of the three samples of *allo*ocimene from natural sources, from synthesis, and from pinene has been rigidly established by preparation of the additive compounds with maleic anhydride and with α-naphthaquinone.[37, 39] The conversion of α-pinene into *allo*ocimene does not pass through the stage of dipentene, the route suggested by Arbusov[37] being as follows :



The pyrolysis of various terpene derivatives at 550° under reduced pressure, including that of carveol, menthoglycol, *iso*pulegyl acetate, and *iso*amyl*iso*pulegol, has been studied by J. Dœuvre.[40]

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[35] *J.*, 1932, 1424, *A.*, 1932, 739.

[36] *J. Gen. Chem. Russia*, 1933, **3**, 21, 28; *A.*, 1933, 717.

[37] *Ber.*, 1934, **67**, [*B*], 563, 569; *A.*, 1934, 658; cf. G. Dupont and R. Dulou, *Compt. rend.*, 1935, **201**, 219; *A.*, 1127.

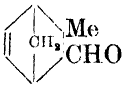
[38] *Ber.*, 1933, **66**, [*B*], 669; *A.*, 1933, 592.

[39] B. A. Arbusov, *Ber.*, 1934, **67**, [*B*], 1946; *A.*, 1935, 89.

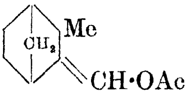
[40] *Bull. Soc. chim.*, 1933, [iv], **53**, 170, 589; 1934, [v], **1**, 198; *A.*, 1933, 612, 1054; 1934, 897.

Santene Group.—Santene (C_9H_{14}) and santenol ($C_9H_{16}O$), which can be isolated from East Indian sandalwood oil, are of particular interest in that they contain one carbon atom less than other monoterpenes and thus constitute an exception to the isoprene rule. It seems very probable, however, that they are secondary products derived from more complex associated compounds found in the same oil, for example, santalol or teresantalic acid (see p. 327).

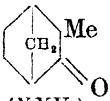
There has been considerable synthetic activity in this group during the last four years, with the result that the structures of santene, santenone, and α-santenol are now firmly established. Early synthetic work by G. Komppa and L. Ruzicka involved Wagner rearrangements. The first direct synthesis was that of O. Diels and K. Alder,[41] based on the " diene " reaction. *cyclo*-Pentadiene was condensed with crotonaldehyde to the aldehyde (XXIII), which after reduction was converted into the enol acetate (XXIV) and thence by ozone into 6-methylnorcamphor (XXV). This could also be prepared by methylation of norcamphor, which had been synthesised similarly from acraldehyde.[42] On treatment with methylmagnesium iodide, (XXV) yielded "γ-santenol" (XXVI), not identical with natural santenol or the known santene hydrate. This was dehydrated to santene (XXVII) and thence converted by the Bertram–Walbaum reagent into α-santenol (XXVIII), both identical with the natural products.



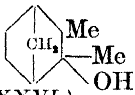
(XXIII.)



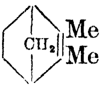
(XXIV.)



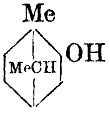
(XXV.)



(XXVI.)



(XXVII.)



(XXVIII.)

O. Aschan had shown that the oxidation of natural santenol or santenone yielded santenic acid. The constitution of this has now been established by independent synthetic work by T. Enkvist [43] and G. Komppa.[44, 45] Both workers used a modification of the Komppa synthesis of camphoric acid, starting with β-methylglutaric ester. This was condensed with oxalic ester to the diketo-ester (XXIX); the synthesis then followed the stages shown below:

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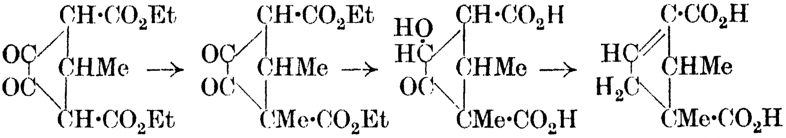
[41] *Annalen*, 1931, **486**, 205; *A.*, 1931, 849.

[42] Further methylation yielded 6 : 6-dimethylnorcamphor (camphenilone), and as this can be converted in turn into camphene, *iso*borneol, and camphor, a new synthetic route to these substances is opened up.

[43] *Finska Kem. Medd.*, 1932, **41**, 74, 85; *J. pr. Chem.*, 1933, [ii], **137**, 261; *A.*, 1933, 273, 822.

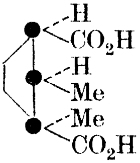
[44] *Ber.*, 1932, **65**, [*B*], 1708; *A.*, 1933, 70.

[45] G. Komppa and W. Rohrmann, *ibid.*, 1934, **67**, [*B*], 828; *A.*, 1934, 889.

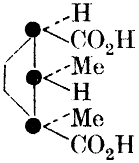


(XXIX.) (XXX.)

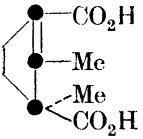
Catalytic reduction of (XXX) yielded *allo*santenic acid,[46] isomeric with santenic acid from natural sources. Both are *cis*-acids convertible into anhydrides and into the respective *trans*-isomerides.[43] If a double bond is introduced into "natural" santenic acid by bromination and dehydrobromination, santenenic acid is formed (Aschan). On reduction, this yields mainly (*cis*-) *allo*-santenic acid, identical with the synthetic product. Enkvist therefore gives "natural" and *allo*-santenic acids the formulæ (XXXI*a* and *b*). The inversion through santenenic acid shows that this is (XXXII). The synthetic acid is probably (XXXI*b*), as it yields an anhydride more readily than does the "natural" acid.[43]



(XXXI*a*.)



(XXXI*b*.)



(XXXII.)

Synthetic *allo*santenic acid can be converted into santenenic acid (XXXII) by bromination and removal of hydrogen bromide. "Natural" santenic acid has been isolated as a by-product in the reduction of santenenic acid and has thus been completely synthesised.[45] Aschan's *iso*santenic acid obtained from α-santenol is a mixture of (*cis*-) santenic and *allo*santenic acids.[43]

By applying the classical method, used by Haller for the synthesis of camphor, to *cis*-santenic anhydride, T. Enkvist has synthesised homosantenic acid (XXXIII; leaflets, m. p. 165°) and santenone (XXXIV). The ring fission of the ketone to homosantenic acid was also achieved by methods successful in the camphor series.[43] A synthesis of homosantenic acid from lævulic ester, resembling Ruzicka's synthesis of fenchone, has been reported.[47]

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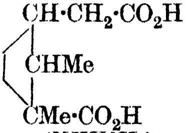
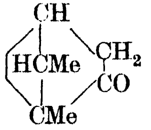
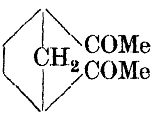
[46] Called *cis-iso*santenic acid by Komppa, but the prefix *allo* (Enkvist) seems preferable, as the name *iso*santenic acid has already been used by Aschan in another connection.

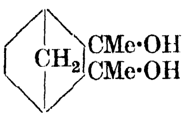
[47] S. C. Sen-Gupta, *J. Indian Chem. Soc.*, 1933, **10**, 341; *A.*, 1933, 1049.

The product (needles, m. p. 170°) may be a stereoisomeride of Enkvist's acid.


(XXXIII.)


(XXXIV.)


(XXXVI.)


(XXXV.)

The structural position has been further consolidated by L. M. Mohunta and J. N. Rây's elegant synthesis [48] of santene glycol (XXXV) from W. H. Perkin's αα-diacetyladipic ester. The disodio-compound of this ester was condensed with methylene iodide, and the product hydrolysed to 1 : 3-diacetyl*cyclo*pentane (XXXVI). This on reduction with aluminium amalgam yielded the glycol (XXXV), identical with that obtained by gentle oxidation of santene. Various reactions in the santene series involving rearrangement of the carbon skeleton have been studied by G. Komppa and G. A. Nyman.[49]

Sesquiterpene Group.

Caryophyllenes.—The three isomeric hydrocarbons of this name occur in oil of cloves.[50] Ozonisation of the mixture, followed by treatment with nitric acid, had given F. W. Semmler and E. W. Mayer [51] a liquid acid which L. Ruzicka, J. C. Bardhan, and A. H. Wind [52] had separated into impure caryophyllenic acid, $C_9H_{14}O_4$, and a norcaryophyllenic acid, $C_8H_{12}O_4$, m. p. 145—150°. Further investigation of these substances by the schools of L. Ruzicka and J. L. Simonsen has given important results. W. C. Evans, G. R. Ramage, and J. L. Simonsen [53] oxidised γ-caryophyllene with potassium permanganate, followed by nitric acid, to a mixture of *as*-dimethylsuccinic acid, *d*-norcaryophyllenic acid, $C_8H_{12}O_4$, m. p. 125—127°, and caryophyllenic acid, $C_9H_{14}O_4$, m. p. 80—81°. Essentially the same substances were obtained by L. Ruzicka and W. Zimmermann [54] by a repetition of the ozonisation experiments, and it was recognised that norcaryophyllenic acid was not a norpinic acid. Norcaryophyllenic acid yielded a dibromo-compound and therefore contained two α-(CH) groups.[54] Bromination and elimination of hydrogen bromide yielded dehydronorcaryophyllenic acid, $C_8H_{10}O_4$, m. p. 194°.[53, 54] L. Ruzicka [54] proposed formulæ

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[48] *J.*, 1934, 1328; *A.*, 1934, 1225.

[49] *Annalen*, 1935, **517**, 105; **518**, 204; *A.*, 865, 983.

[50] Early work in this field is summarised by J. L. Simonsen, *op. cit.*, II, 513.

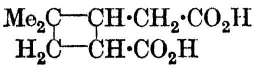
[51] *Ber.*, 1911, **44**, 3657; *A.*, 1912, i, 120.

[52] *Helv. Chim. Acta*, 1931, **14**, 423; *A.*, 1931, 734.

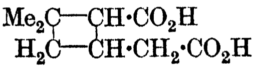
[53] *J.*, 1934, 1806; *A.*, 1935, 90.

[54] *Helv. Chim. Acta*, 1935, **18**, 219; *A.*, 351.

(XXXVI*a* or *b*) for caryophyllenic acid and (XXXVII) for norcaryophyllenic acid :

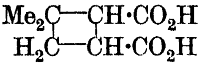


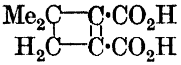
(XXXVI*a*.)



(XXXVI*b*.)

(XXXVII.)





(XXXVIII.)

The relationship between caryophyllenic acid and its lower homologue was established by G. R. Ramage and J. L. Simonsen [55] by a degradation similar to that of pinic acid effected by Baeyer. In the same paper, dehydronorcaryophyllenic acid was shown to have formula (XXXVIII) by ozonisation to α′-keto-αα-dimethylglutaric acid. The formulæ (XXXVII) and (XXXVIII) have been confirmed by H. N. Rydon's synthesis [56] of dehydronorcaryophyllenic and *dl*-norcaryophyllenic acids, the latter being identical with an inactive acid, m. p. 148—149°, isolated by Ramage and Simonsen during the preparation of the dehydro-acid. The stereochemistry of norcaryophyllenic acid is not yet clear. The "natural" *d*-acid, m. p. 125—127°, is presumably *cis*-, as it gives a liquid anhydride, from which it is regenerated,[53] but Ruzicka and Zimmermann state [54] that the action of acetic anhydride at 220° on norcaryophyllenic acid yields a solid anhydride which gives an acid of m. p. 149—150°. H. N. Rydon [57] has isolated two distinct (*cis*- and *trans*-) racemic acids, both of which melt at about 149°. It seems probable to the Reporter that Ramage and Simonsen's inactive acid (148—149°) is the *trans*-acid, and Ruzicka and Zimmermann's the *dl*-*cis*-acid, having been racemised during the formation of the anhydride.

The structure of the rest of the caryophyllene molecule is not yet certain. For the principal constituent of the natural terpenes (β-isomeride), L. Ruzicka [58] has proposed formula (XXXIX), which explains the formation of the above acids and the step-wise degradations studied by himself and A. H. Wind.[59] The ozonolysis of β-caryophyllene nitrosite also can be explained on this basis, although G. R. Ramage and J. L. Simonsen [60] point out that formula (XL) is equally satisfactory. A number of difficulties remain to be explained, including the isomerisation of caryophyllene to the tricyclic clovene, which can be oxidised to the remarkably stable clovenic acid ($C_{15}H_{24}O_4$) without loss of carbon.[61]

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[55] *J.*, 1935, 532; *A.*, 756; cf. *idem*, *Chem. and Ind.*, 1935, **54**, 151; *A.*, 489.

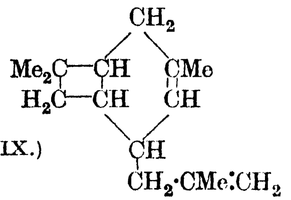
[56] *Chem. and Ind.*, 1935, **54**, 557.

[57] Private communication.

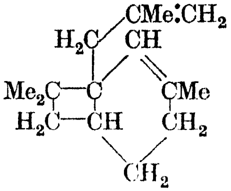
[58] *Chem. and Ind.*, 1935, **54**, 509; *A.*, 866.

[59] *Helv. Chim. Acta*, 1931, **14**, 410; *A.*, 1931, 734.

[60] *J.*, 1935, 1581.

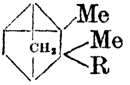


(XXXIX.)

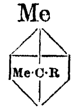


(XL.)

Santalols and Santalenes.—East Indian sandalwood oil contains two sesquiterpenes, α- and β-santalenes, and two important sesquiterpene alcohols, α- and β-santalols. The α-compounds are tricyclic and their structure (Type XLI) has been established mainly by Semmler. They can be degraded to teresantalic acid (XLI; R = CO_2H), which is itself present in sandalwood oil.



or

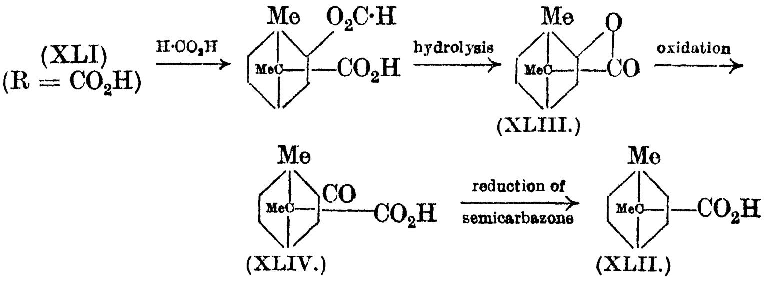


(XLI*a*.) (XLI*b*.)

α-Santalol, R = $[CH_2]_2\cdot CH{:}CMe\cdot CH_2\cdot OH$
α-Santalene, R = $[CH_2]_2\cdot CH{:}CMe_2$

[These are different projections of the same formula.[62]]

The structure of teresantalic acid has now been confirmed by its conversion[63] by T. Hasselström into dihydroteresantalic acid, identical with his synthetic 7-π-apocamphanecarboxylic acid (XLII). This was accomplished by fission of the *cyclo*propane ring with hydrochloric acid, followed by reduction with sodium and alcohol, or through the lactone (XLIII) of F. W. Semmler and K. Bartelt,[64] as follows :



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[61] R. D. Blair, *J.*, 1935, 1297; *A.*, 1375.

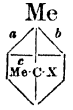
[62] L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1922, **5**, 928; *A.*, 1923, i, 119; cf. *Ann. Reports*, 1927, **24**, 121.

[63] *J. Amer. Chem. Soc.*, 1931, **53**, 1097; *A.*, 1931, 626.

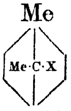
[64] *Ber.*, 1907, **40**, 4465; *A.*, 1907, i, 1062.

Teresantalic acid has been synthesised [65] from *iso*ketopinic acid (XLIV) by oxidation of the hydrazone with mercuric oxide in alcoholic potash. The *iso*teresantalic acid of H. Rupe and W. Tomi [66] is now regarded as a structural rather than a stereoisomeride.[65]

β-Santalol and β-santalene are closely related to the isomeric α-compounds, but are dicyclic. Their structure is still unsettled, though considerable progress has been made. A. E. Bradfield, A. R. Penfold, and J. L. Simonsen [67] have separated pure α- and β-santalol from the oil from *Santalum album* and have confirmed the fact that they contain the same fundamental structure. α-Santalol was converted through the chloride into α-santalylmalonic ester and acid [XLI; R = $-(CH_2)_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CH(CO_2H)_2$], which on hydrogenation and decarboxylation yielded dihydro-α-santalylacetic acid (XLV). The *cyclo*propane ring in this compound was reduced by successive treatment with hydrogen bromide and sodium in alcohol, the product being tetrahydrosantalylacetic acid. By analogy with T. Hasselström's synthesis this is given formula (XLVI), bond *c* being broken.[68]



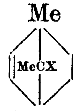
(XLV.)



(XLVI.)

[X = $-(CH_2)_3{\cdot}CHMe{\cdot}(CH_2)_2{\cdot}CO_2H$]

By similar treatment, β-santalol yielded β-santalylmalonic acid, which on hydrogenation and decarboxylation gave the same dicyclic acid (XLVI). Bradfield, Penfold, and Simonsen give β-santalol the formula (XLVII), since the double bond cannot be attached to the bridge-head.



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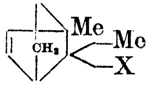

(XLVII*a*.) (XLVII*b*.)

[X = $\cdot(CH_2)_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}OH$ for β-santalol]

L. Ruzicka and G. Thomann's experiments,[69] on the other hand, have led to a different conclusion. F. W. Semmler [70] had degraded β-santalene to *bicyclo*ekasantalic acid, $C_{12}H_{18}O_2$. Ruzicka and Thomann ozonised this to a keto-acid, $C_{11}H_{16}O_3$ (XLVIII), and a lactonic acid, $C_{11}H_{16}O_4$ (XLIX). The second of these was also obtained by direct ozonolysis of crude santalol or santalene, both rich in β-compounds (this actually appears to provide the first evidence that β-santalol is a hydroxy-derivative of β-santalene). The β-series of compounds is therefore given the basic formula (L) and the degradation is interpreted as follows :

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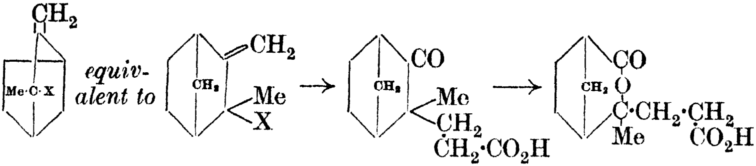
[65] Y. Asahina, M. Ishidate, and T. Momose, *Ber.*, 1935, **68**, [*B*], 83; *A.*, 350.

[66] *Ibid.*, 1916, **49**, 2563; *A.*, 1917, i, 138.

[67] *J.*, 1935, 309; *A.*, 315.

[68] There is a slight error in Bradfield, Penfold, and Simonsen's paper (*loc. cit.*, p. 311). It is stated that fission of bonds *a* and *b* in (XLV) would lead to structurally identical but enantiomorphous substances. Actually the substances so formed would be *cis-trans*-isomerides, not enantiomorphs. This does not affect the main argument.

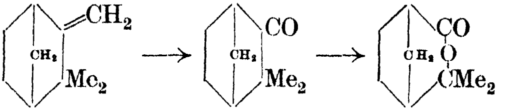
[69] *Helv. Chim. Acta*, 1935, **18**, 355; *A.*, 625.



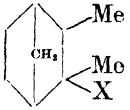
(L*a*.) (L*b*.) (XLVIII.) (XLIX.)

[X = $\cdot(CH_2)_2\cdot CH{:}CMe\cdot CH_2OH$, β-santalol.
X = $\cdot(CH_2)_2\cdot CH{:}CMe_2$, β-santalene.
X = $\cdot(CH_2)_2\cdot CO_2H$, *bicyclo*ekasantalic acid.]

Ruzicka and Thomann draw a suggestive analogy between this ozonolysis and that whereby camphene (LI) is converted into camphenilone (LII) and dimethylnorcampholide [71] (LIII). On this basis, α- and β-santalenes stand in the same relationship as tricyclene and camphene.



(LI.) (LII.) (LIII.)



(LIV.)

The Simonsen and the Ruzicka formula (XLVII and L) thus contain the same carbon skeleton, but differ in the arrangement of the double bond and rings. If Ruzicka's formula for β-santalol were correct, tetrahydrosantalylacetic acid would be of type (LIV). This would mean that the *cyclo*propane ring of dihydro-α-santalylacetic acid would open in a different manner from that of teresantalic acid. There seems to be no reason why this should happen and it does not appear possible to reconcile the two sets of experiments except by postulating either that both forms are present or that the initial material of the two investigations was different.

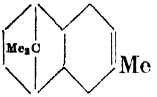
Cedrene.—Interest in this tricyclic sesquiterpene has been reawakened by the experiments of W. Treibs.[72] The most important

[70] *Ber.*, 1907, **40**, 3323; *A.*, 1907, i, 781.

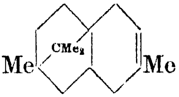
[71] C. D. Harries and J. Palmén, *ibid.*, 1910, **43**, 1432; *A.*, 1910, i, 497.

[72] *Ibid.*, 1935, **68**, [*B*], 1041; *A.*, 983.

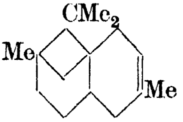
new results are (i) that cedrene, passed over nickel at 420—450°, gives some 30% of *p*-cymene; and (ii) that oxidation of cedrene with permanganate, followed by nitric acid, yields trimethylsuccinic acid and an acid, probably but not certainly camphoronic acid. From these facts and those already known, Treibs has proposed formula (LV) for cedrene. This, however, is not acceptable, as pointed out by W. F. Short,[73] for it does not accommodate the degradation of norcedrenedicarboxylic acid to cedrenecamphoric acid ($C_{10}H_{16}O_4$), observed by L. Ruzicka and J. A. van Melsen,[74] which involves a loss of three carbon atoms. Short has advanced formula (LVI). The evidence has been reviewed by R. Robinson and J. Walker,[75] who have proposed formulæ (LVII) and (LVIII), the second of which appears the most acceptable of those in the field.



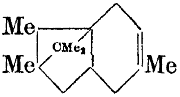
(LV.)



(LVI.)



(LVII.)



(LVIII.)

Formula (LVI) requires that cedrenecamphoric acid should be identical with camphoric acid or a stereoisomeride; formulæ (LVII) and (LVIII) that it should be a methylpinic or a dimethylnorpinic acid respectively. As Ruzicka's acid was a liquid, the first of these possibilities is unlikely; neither of the other acids is available for comparison.

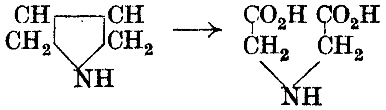
R. P. L.

7. HETEROCYCLIC COMPOUNDS.

Nitrogen Ring Compounds.

A. Treibs and D. Dinelli[1] have settled a point which has long caused difficulty, namely, the position of the double bond in pyrroline (obtained by reducing pyrrole with zinc or iron and acetic acid). They find that ozonolysis of pyrroline hydrochloride in aqueous solution, followed by oxidation with hydrogen peroxide, gives iminodiacetic acid (I), thus establishing beyond doubt that pyrroline is (II).

(II.)



(I.)

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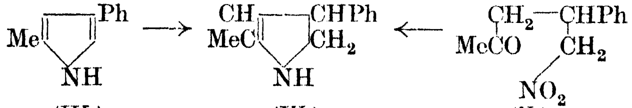
[73] *Chem. and Ind.*, 1935, **54**, 874; *A.*, 1376.

[74] *Annalen*, 1929, **471**, 40; *A.*, 1929, 932.

[75] *Chem. and Ind.*, 1935, **54**, 906, 946; *A.*, 1503.

[1] *Annalen*, 1935, **517**, 170; *A.*, 868.

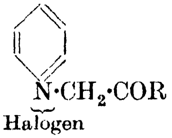
The course of the reduction of substituted pyrroles is, however, determined by the nature of the substituents present. For instance,[2] the product of the reduction of 4-phenyl-2-methylpyrrole (III) by iron (or zinc) and acetic acid is (IV), since it is identical with the product obtained by the reduction of methyl γ-nitro-β-phenylpropyl ketone (V).



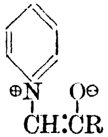
(III.) (IV.) (V.)

During the scission of additive compounds of type (VI) by means of alkali, yellow to red intermediate compounds are formed, and are isolable when cold alkali carbonate is used. These compounds are given [3] the "enol-betaine" structure (VII).

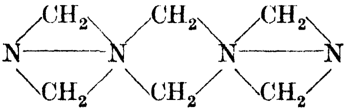
M. Dominikiewicz,[4] from a study of some acylation reactions with hexamethylenetetramine, concludes that this substance has the structure (VIII), but this appears to be at variance with *X*-ray evidence,[5] which supports the usually accepted formula due to P. Duden and M. Scharff.[6]



(VI.)



(VII.)



(VIII.)

Alkaloids.

Pilocarpine.—*dl*-Pilopic acid (two forms) (I) was synthesised by A. E. Tschitschibabin and N. A. Preobrashenski,[1] who, having shown that Jowett's pilopic (pilopinic) acid [2] is configuratively related not to pilocarpine but to *iso*pilocarpine, named it *d-iso*-pilopic acid, reserving the name *d*-pilopic for the labile acid corresponding to the labile pilocarpine. K. N. Welch [3] independently synthesised *dl*-pilopic acid by a different process. Some time ago,[4]

[2] A. Sonn, R. Podschus, K. Schützler, and G. Stephani, *Ber.*, 1935, **68**, [*B*], 148; *A.*, 355.

[3] F. Kröhnke, *ibid.*, p. 1177; *A.*, 987.

[4] *Arch. Chem. Farm.*, 1935, **2**, 78; *A.*, 762.

[5] R. G. Dickinson and A. L. Raymond, *J. Amer. Chem. Soc.*, 1923, **45**, 22; *A.*, 1923, i, 308. See also H. W. Gonell and H. Mark, *Z. physikal. Chem.*, 1923, **107**, 181; *A.*, 1924, i, 150.

[6] *Annalen*, 1895, **288**, 218; *A.*, 1896, i, 122.

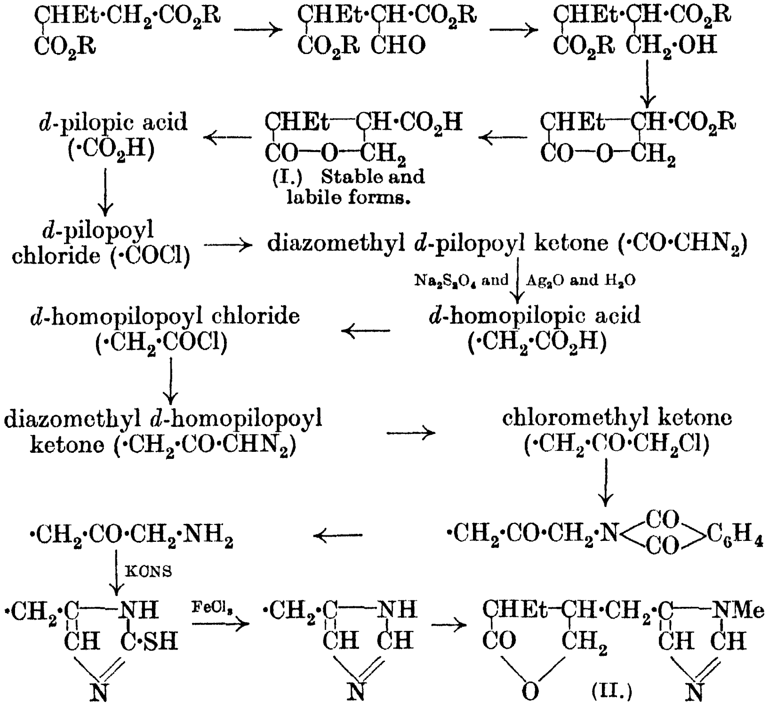
[1] *Ber.*, 1930, **63**, [*B*], 460; *A.*, 1930, 452.

[2] *J.*, 1903, **83**, 463.

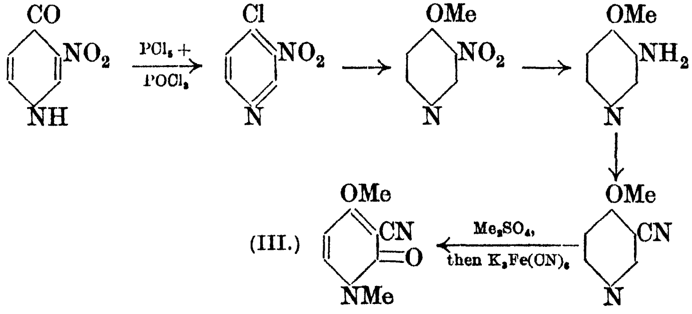
[3] *J.*, 1931, 1370.

[4] N. A. Preobrashenski, A. F. Wompe, V. A. Preobrashenski, and M. N. Schtschukina, *Ber.*, 1933, **66**, [*B*], 1536; *A.*, 1933, 1311.

d-homopilopic acid was used as a starting point for the synthesis of pilocarpine, and recently [5] *d*-homopilopic acid has been synthesised; so the complete synthesis of the alkaloid (II) has been effected:


CHEt·CH$_2$·CO$_2$R
CO$_2$R
CHEt·CH·CO$_2$R
CO$_2$R CHO
CHEt·CH·CO$_2$R
CO$_2$R CH$_2$·OH
CHEt—CH·CO$_2$R
CO—O—CH$_2$
CHEt—CH·CO$_2$H
CO—O—CH$_2$
(I.) Stable and labile forms.
d-pilopic acid (·CO$_2$H)
d-pilopoyl chloride (·COCl)
diazomethyl *d*-pilopoyl ketone (·CO·CHN$_2$)
Na$_2$S$_2$O$_4$ and
Ag$_2$O and H$_2$O
d-homopilopic acid (·CH$_2$·CO$_2$H)
d-homopilopoyl chloride (·CH$_2$·COCl)
diazomethyl *d*-homopilopoyl ketone (·CH$_2$·CO·CHN$_2$)
chloromethyl ketone (·CH$_2$·CO·CH$_2$Cl)
·CH$_2$·CO·CH$_2$·N<CO CO>C$_6$H$_4$
·CH$_2$·CO·CH$_2$·NH$_2$
KCNS
·CH$_2$·C—NH CH C·SH N
FeCl$_3$
·CH$_2$·C—NH CH CH N
CHEt—CH·CH$_2$·C—NMe CO CH$_2$ O CH CH N
(II.)

Ricinine.—A new synthesis of this alkaloid (III) has been described by J. Reitmann: [6]



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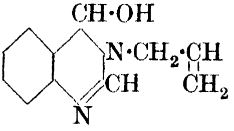
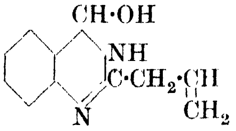
[5] N. A. Preobrashenski, A. M. Poljakova, and V. A. Preobrashenski, *Ber.*, 1935, **68**, [*B*], 850; *A.*, 872.

[6] *Med. Chem. Abh. med.-chem. Forschungsstätten I. G. Farbenind.*, 1934, **2**, 384; *A.*, 1935, 97. See *Ann. Reports*, 1923, **20**, 153.

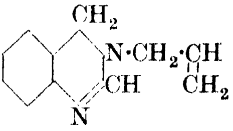
Peganine and *Vasicine*.—E. Späth and E. Nikawitz [7] assigned to peganine the structure (IV), and the former author, with F. Kuffner,[8] stated that peganine and vasicine were identical. K. S. Narang and J. N. Rây [9] regarded vasicine as being (V), and denied the identity of the alkaloids. (Miss) T. M. Reynolds and R. Robinson [10] synthesised a compound of structure (IV) and found that it was not identical with vasicine.



(IV.)



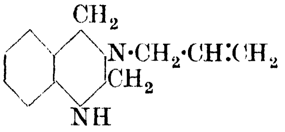
(V.)

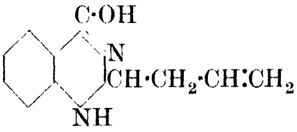


(VI.)

W. E. Hanford, P. Liang, and R. Adams [11] showed that reduction of 3-allyl-3 : 4-dihydroquinazoline (VI), which was not identical with deoxyvasicine, or of the 4-keto-derivative of (VI) gave compound (VII), which, in turn, was not identical with dihydrodeoxyvasicine.

(VII.)

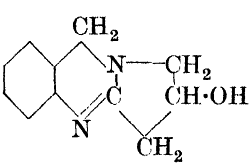


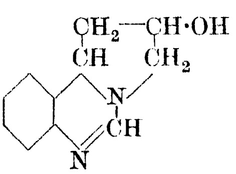


(VIII.)

From this, it followed that vasicine could not be (IV), (VIII), or (V). Dihydrodeoxyvasicine was prepared by the Späth–Nikawitz method of obtaining dihydrodeoxypeganine (called by Späth and Nikawitz deoxytetrahydropeganine), and shown to be identical with the latter substance. Vasicine and peganine were therefore regarded as being identical, either (IX) or (X).

(IX.)





(X.)

E. Späth, F. Kuffner, and N. Platzer [12] confirmed the physical identity of purified peganine and vasicine, and carried out the following conversions :

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[7] *Ber.*, 1934, **67**, [*B*], 45; *A.*, 1934, 310.

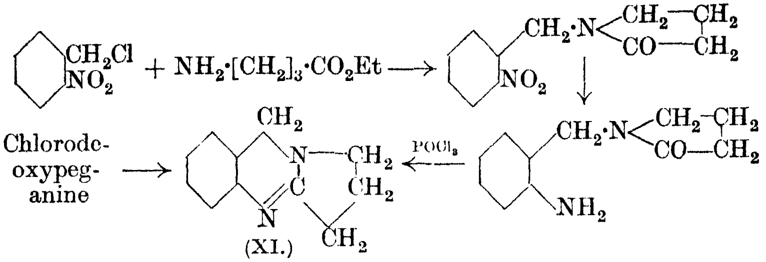
[8] *Ibid.*, p. 868; *A.*, 1934, 787.

[9] *Chem. and Ind.*, 1934, 698; *A.*, 1934, 1014.

[10] *Nature*, 1934, **134**, 142; *A.*, 1934, 1014.

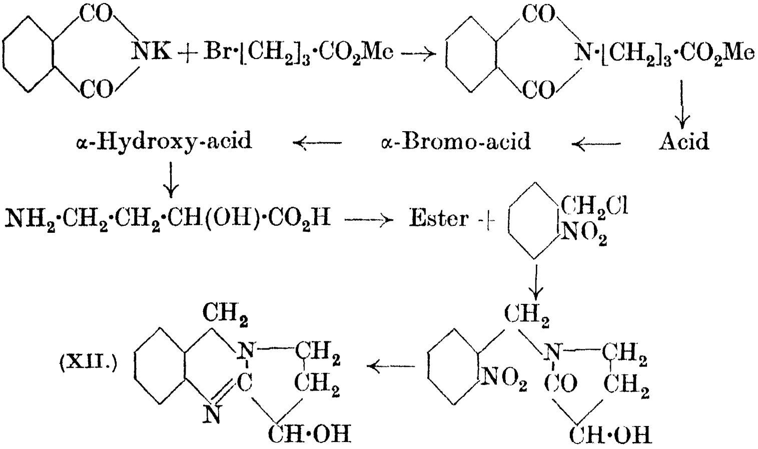
[11] *J. Amer. Chem. Soc.*, 1934, **56**, 2780; *A.*, 1935, 365.

[12] *Ber.*, 1935, **68**, [*B*], 497; *A.*, 635.

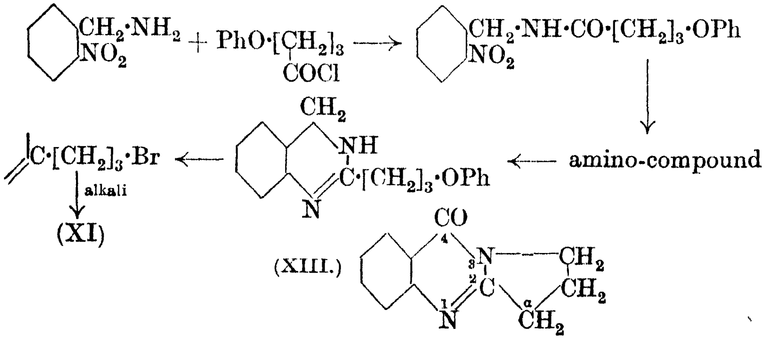


from which it followed that peganine was a hydroxy-derivative of (XI).

The same authors [13] then effected a synthesis of peganine (XII):



W. E. Hanford and R. Adams,[14] in an endeavour to obtain further experimental evidence in favour of formula (IX), also synthesised the above base (XI), which they identified with deoxyvasicine:



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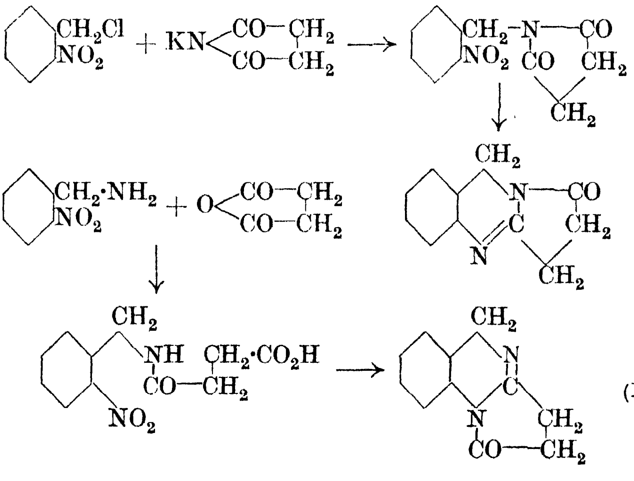
[13] *Ber.*, 1935, **68**, [*B*], 699; *A.*, 764.

[14] *J. Amer. Chem. Soc.*, 1935, **57**, 921; *A.*, 873.

These authors, in conjunction with R. C. Morris,[15] studied afresh the oxidation of vasicine by hydrogen peroxide, obtaining results different from those in the literature.[16] They synthesised the compound (XIII), which was also obtained by oxidation of deoxyvasicine with hydrogen peroxide, and oxidised it by means of lead tetra-acetate to an acetoxy-compound. This, when saponified, gave a product identical with one of the compounds described by Ghose and his co-workers.[16] Since (XIII) contains a carbonyl group in position 4, they concluded that the hydroxyl group must have entered the α-position, this being the most activated. It was therefore reasoned that vasicine was (XII).

This reasoning, though not its consequences, was criticised by E. Späth, F. Kuffner, and N. Platzer.[17] These authors resolved peganine with *d*(and *l*)-tartaric acid and showed it to be fairly easily racemised. Ghose and his co-workers [16] had already stated, without evidence, that vasicine "was resolvable." The German authors suggest that the peganine in *Peganum harmala* (where it is associated with harmine, harmaline, and harmalol) is optically active, but that it undergoes racemisation during its extraction.

H R. Juneja, K. S. Narang, and J. N. Rây,[18] who by inference still do not admit the identity of peganine and vasicine, also obtained proof of the constitution of the latter. Bases (XIV) and (XV) were synthesised according to the following schemes :


(XIV.)

(XV.)

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[15] *J. Amer. Chem. Soc.*, 1935, **57**, 951; *A.*, 873.

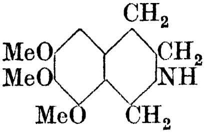
[16] T. P. Ghose, S. Krishna, K. S. Narang, and J. N. Rây, *J.*, 1932, 2740; *A.*, 1933, 77.

[17] *Ber.*, 1935, **68**, [*B*], 1384; *A.*, 1136.

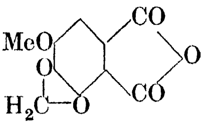
[18] *J.*, 1935, 1277; *A.*, 1387.

Since vasicine and (XIV) on electrolytic reduction gave one and the same substance, which was different from the reduction product from (XV), vasicine must be (XII).

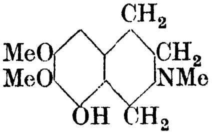
Cactus Alkaloids.—E. Späth and F. Becke [19] have isolated the new alkaloid, anhalinine, from *Anhalonium Lewinii*, and shown it to be (XVI), identical with the product of condensing mezcaline with formaldehyde. The constitution of anhalonine is further confirmed as follows : The alkaloid is converted by methyl iodide and sodium methoxide into methylanhalonine methiodide; the corresponding methohydroxide is oxidised to *iso*cotarnic acid, isolated as the anhydride (XVII). The structure of the latter has already been proved by synthesis.[20]



(XVI.)



(XVII.)



(XVIII.)

Yet another alkaloid, anhalidine, is present [21] in the above material. Its constitution (XVIII) is established by its formation by the action of methyl-alcoholic methyl iodide on anhalamine. In the mezcal buttons actually examined, anhalamine, anhalinine, and anhalidine were present to the extent of about 0·1, 0·01, and 0·001%, respectively, in addition to anhalonidine, pellotine, mezcaline, and lophophorine.

The synthetic work in this series has been extended [22] by the optical resolution of *dl*-anhalonine, the *l*-base being identical with the natural alkaloid. Formaldehyde–formic acid methylation of the *l*-base gave *N*-methyl-*l*-anhalonine, identical with (the liquid) lophophorine. This completes the synthesis of all the bases present in this species of cactus.

iso*Quinoline Derivatives.*—G. Hahn and O. Schales [23] have shown that β-phenylethylamines containing methoxy- or methylenedioxy-groups in the nucleus condense with phenylacetaldehydes or phenylpyruvic acids under physiological conditions, though condensation is slower than with the hydroxy-compounds. The most favourable p_H for the first stage of the condensation $RR'CO + NH_2R'' \longrightarrow$

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[19] *Ber.*, 1935, **68**, [*B*], 501; *A.*, 635.

[20] E. Späth, L. Schmid, and H. Sternberg, *Ber.*, 1934, **67**, [*B*], 2095; *A.*, 1935, 213.

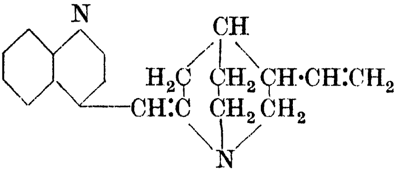
[21] E. Späth and F. Becke, *Ber.*, 1935, **68**, [*B*], 944; *A.*, 873.

[22] E. Späth and F. Kesztler, *ibid.*, p. 1663; *A.*, 1389.

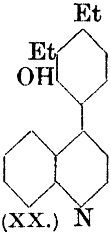
[23] *Ibid.*, p. 24; *A.*, 357. See also E. Späth and F. Kuffner, *ibid.*, p. 1744.

$RR'C(OH)\cdot NHR''$ or $RR'C\colon NR''$ is 5; $RR'CO$ may be an aldehyde or a keto-acid and R'' may be an amine or an amino-acid.

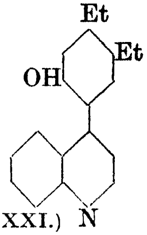
Cinchona Alkaloids.—A piece of work which all who have been interested in cinchona alkaloids will welcome is that by J. Kenner and F. S. Statham.[24] Cinchene (XIX), when heated for a long period with hydrobromic acid, is converted into apocinchene, which Koenigs originally showed to be either (XX) or (XXI).



(XIX.)

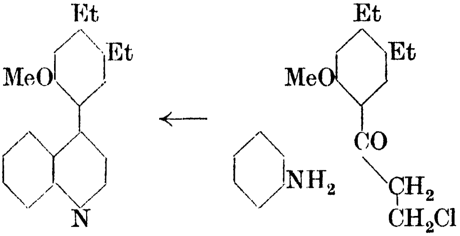


(XX.)

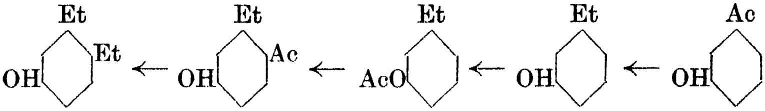


(XXI.)

The above authors preferred the second alternative, and synthesised the corresponding methyl and ethyl ethers, the picrates of which proved to be identical with those of the apocinchene ethers :



The substituted propiophenone was prepared from 3 : 4-diethylanisole and β-chloropropionyl chloride, the preceding stages being as shown below :



As the authors admit, the mechanism of the cinchene → apocinchene change remains obscure, but they have now provided the material upon which any theory of that change must be built.

The doubt which has existed for a very long time as to the nature of the products obtained by demethylating quinine has caused T. A. Henry and W. Solomon[25] to investigate the problem. They find that demethylation with aluminium chloride gives, not "apo-

[24] *J.*, 1935, 299; *A.*, 766.

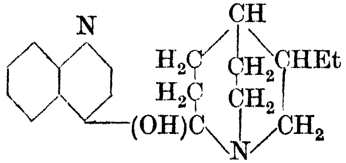
[25] *J.*, 1934, 1923; *A.*, 1935, 227.

quinine,"[26] $C_{19}H_{22}O_2N_2$, but this substance mixed with chlorodihydroapoquinine, $C_{19}H_{23}O_2N_2Cl$. Demethylation of quinine[27] and of quinidine[28] by means of boiling 60% sulphuric acid has been investigated by previous authors, and their methods have been improved. Henry and Solomon show that Suszko's apoquinine is readily purified, and that his method provides a convenient source of the substance, but they could not obtain his " cupreidine " from quinidine. Instead, two products, *iso*apoquinidine and apoquinidine, were isolated. In a later paper,[29] it is shown that the products of demethylating quinine with sulphuric acid include apoquinine, *iso*apoquinine, and hydroxydihydroapoquinine; and from quinidine an individual apoquinidine was definitely obtained in addition to *iso*apoquinidine.[30] Undemethylated products also have been characterised.

H. Thron and W. Dirschel[31] separated cinchona alkaloids (from their dihydro-derivatives) as the compounds $R{\cdot}CH(HgOH){\cdot}CH_2{\cdot}OH$, and also studied alkaloid demethylation with sulphuric acid.

In last year's Reports (p. 272) it was noted that Rabe had criticised Suszko's formula for epicinchonine. R. Ludwiczakówna and J. Suszko[32] recognise the correctness of Rabe's proposed formula, and obtain a substance of analogous structure (XXII) by treating dihydrocinchonine successively with *p*-toluenesulphonyl chloride, n pyridine, and potassium benzoate, and hydrolysing the product. The name *hetero*dihydrocinchonine is applied.

(XXII.)



Lycoris *Alkaloids.*—The view, on physiological grounds, that lycorine contains the phenanthridine skeleton has now been confirmed.[33] The base affords phenanthridine when it is distilled with zinc dust, and this possibly doubtful evidence is substantiated in the following manner: Lycorine anhydromethine is oxidised to a mixture of acids, one, which is therefore an α-keto-acid, being oxidised by alkaline hydrogen peroxide to the other. Decarboxylation of the simpler acid gives 6 : 7-methylenedioxy-10-methylphenanthridone (XXIII), which has been synthesised according to the scheme:

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[26] M. Oberlin, *Arch. Pharm.*, 1927, **265**, 269; *A.*, 1927, 681.

[27] L. Jarzyński, R. Ludwiczakówna, and J. Suszko, *Rec. trav. chim.*, 1933, **52**, 839; *A.*, 1933, 1312.

[28] R. Ludwiczakówna, J. Suszko, and R. Zwierzchowski, *ibid.*, p. 847; *A.*, 1933, 1312.

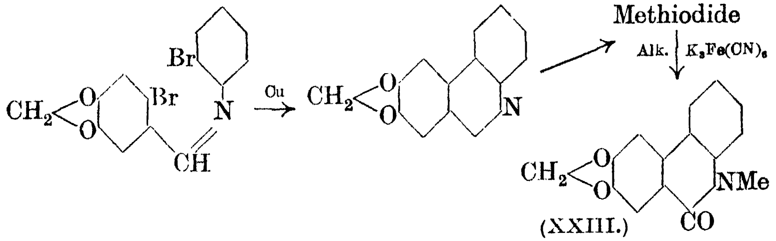
[29] *J.*, 1935, 966; *A.*, 1136. See also C. L. Butler and L. H. Cretcher, *J. Amer. Chem. Soc.*, 1935, **57**, 1083; *A.*, 995; T. A. Henry and W. Solomon, *Chem. and Ind.*, 1935, **54**, 641; *A.*, 995.

[30] See also (Mlle.) R. Ludwiczak and J. Suszko, *Bull. Acad. polonaise*, 1935, [*A*], 65; *Rocz. Chem.*, 1935, **15**, 209; *A.*, 996.

[31] *Annalen*, 1935, **515**, 252; *A.*, 366.

[32] *Arch. Chem. Farm.*, 1935, **2**, 196; *A.*, 765.

[33] H. Kondo and S. Uyeo, *Ber.*, 1935, **68**, [*B*], 1756; *A.*, 1387.



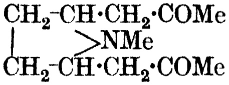
(XXIII.)

Tropan Derivatives.—C. Schöpf and G. Lehmann had already[34] shown that, whereas *o*-aminobenzaldehyde condensed with β-keto-acids under strongly alkaline conditions (p_H 13), under "physiological conditions" (p_H 5—9) the condensation was accompanied by loss of carbon dioxide. It was therefore to be expected that tropinone would be formed when succinaldehyde, methylamine, and acetonedicarboxylic acid were brought together under the second set of conditions. This is now shown[35] to be a fact. In three days at 25°, yields of tropinone of 47, 54, 65, 66, 86, and 3% were obtained at p_H 3, 5, 7, 9, 11, and 13, respectively. At p_H 3, tropinonedicarboxylic acid appears to be formed in excellent yield. Acetone cannot take the place of its dicarboxylic acid in these new condensations, and ethyl acetonecarboxylate (acetoacetic ester) gives 2 : 5-diacetonyl-1-methylpyrrolidine (XXIV). R. Robinson[36] considered that in the biological synthesis of the derivatives of ecgonine, tropinonedicarboxylic acid was formed first, and then underwent loss of one molecule of carbon dioxide. Schöpf and Lehmann regard tropinone as the first stage, and attribute the formation of ecgonine (in reality of tropinonecarboxylic acid) to the use by the plant of methyl hydrogen acetonedicarboxylate. This view is supported by experimental facts. Similarly, the optically inactive teloidine[37] (XXV) is derivable from *meso*tartardialdehyde.

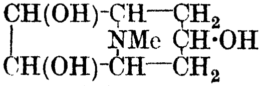
ψ-Pelletierine is formed in good yield in a few days at 25° from glutardialdehyde, methylamine, and acetonedicarboxylic acid at

[34] *Annalen*, 1932, **497**, 7; *A.*, 1932, 1046.
[35] *Ibid.*, 1935, **518**, 1; *A.*, 873.
[36] *J.*, 1917, **111**, 880.
[37] H. King, *J.*, 1919, **115**, 487.

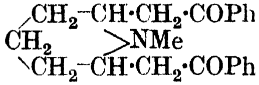
p_H 3—7. The condensation of glutardialdehyde, methylamine, and benzoylacetic acid is more sensitive to hydrogen-ion concentration than are the above condensations. The best yield of



(XXIV.)



(XXV.)



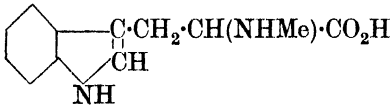
(XXVI.)

lobelanine (XXVI) is obtained at p_H 4, and little condensation occurs at p_H 2 or 7. In alkaline solution (p_H 7—13), lobelanine undergoes hydrolytic scission. In all these condensations it is usually accompanied by a by-product, which is thought to be the *trans*-base. The results on the whole are considered to be excellent evidence for the correctness of Robinson's plan of phytochemical synthesis.

Alkaloids of Convolvulus Pseudocantabricus.—A. Orekhov and R. Konovalova [38] isolated convolvine from the seeds of this plant, and later,[39] convolvamine. The latter, when hydrolysed with alcoholic potassium hydroxide, gives veratric acid and tropine, and is formed when tropine is veratroylated. It is therefore veratroyltropeine. Recently, with E. Eremina,[40] the same authors isolated two further alkaloids, convolvidine and convolvicine, and showed that convolvine is norconvolvamine, *i.e.*, veratroylnortropeine. Nortropine, hitherto difficult of access, is now readily obtainable by the hydrolysis of convolvine.

Abrine.—This is an amino-acid present in the seeds of *Abrus precatorius*, and has been shown by T. Hoshino [41] to be α-methylamino-β-3-indolylpropionic acid (XXVII).

(XXVII.)



Yohimbine.—C. Scholz [42] has shown that tetrahydroyobyrine, previously regarded as having the complete ring structure of yobyrine, is (XXVIII). Ozonolysis produces a base, $C_{19}H_{20}O_2N_2$, probably (XXIX), which is (*a*) hydrolysed (10*N*-sulphuric acid at the b. p.) to *o*-aminopropiophenone and 5 : 6 : 7 : 8-tetrahydro*iso*quinoline-3-carboxylic acid, and (*b*) oxidised to berberonic acid, also known to be obtainable by direct oxidation of tetrahydroyobyrine itself. Whereas oxidation of yobyrine with potassium permanganate gives phthalic acid, oxidation with chromic acid gives, in addition, *o*-toluic acid (pointing to a methylene group in

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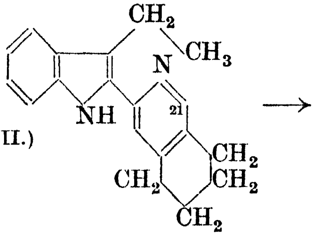
[38] *Arch. Pharm.*, 1933, **271**, 145; *A.*, 1933, 517.

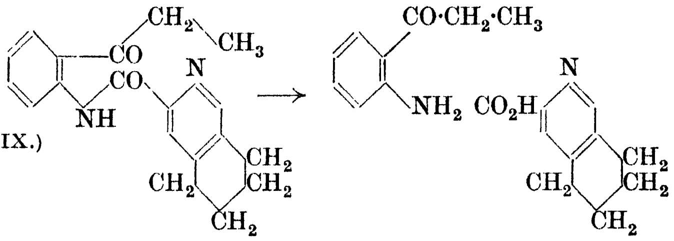
[39] *Ber.*, 1934, **67**, [*B*], 1153; *A.*, 1934, 908.

[40] *Ber.*, 1935, **68**, [*B*], 814; *A.*, 872.

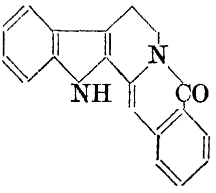
[41] *Proc. Imp. Acad. Tokyo*, 1935, **11**, 227; *A.*, 1131.

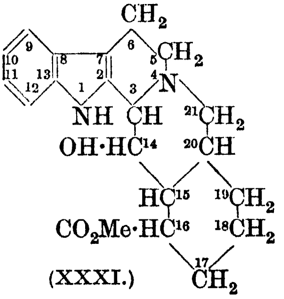
[42] *Helv. Chim. Acta*, 1935, **18**, 923; *A.*, 1138.


(XXVIII.)


(XXIX.)

position 21) and a new substance, oxoyobyrine, which is probably (XXX). The results support the formula (XXXI) for yohimbine.


(XXX.)


(XXXI.)

Raymond-Hamet [43] found that when (lævorotatory) corynanthine was heated with alcoholic potassium hydroxide, a substance was formed which was converted by methyl-alcoholic hydrogen chloride into the hydrochloride of a dextrorotatory ester, which he named ψ-corynanthine. Yohimbine, on the other hand, underwent no stereoisomeric change. C. R. Scholz [44] showed that ψ-corynanthine is a methyl yohimboate and therefore that corynanthine and yohimbine are stereoisomerides, both being convertible into the apoyohimbine described by G. Barger and (Miss) E. Field.[45]

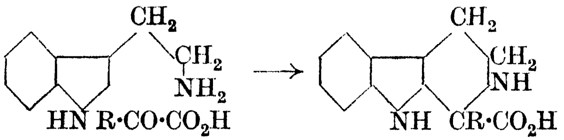
In continuation of their interesting studies on condensation

[43] *Compt. rend.*, 1934, **199**, 1658; *A.*, 1935, 365.

[44] *Ibid.*, 1935, **200**, 1624; *A.*, 995.

[45] *J.*, 1923, **123**, 1038.

"under physiological conditions," G. Hahn, L. Bärwald, O. Schales, and H. Werner[46] find that α-keto-acids condense more readily than the corresponding aldehydes with tryptamine, good yields of norharmans (XXXII) being obtained only with two aldehydes, acetaldehyde and phenylacetaldehyde. Homopiperonal and 3 : 4 : 5-trimethoxyphenylacetaldehyde give only 15 and 20% yields, respectively. Again, under these conditions benzaldehyde gives a 48% yield, but *o*- and *p*-hydroxybenzaldehyde, piperonal, and vanillin do not react appreciably; nor do glyoxal, methylglyoxal, glucose, and citral. Pyruvic acid gives 47, 59, 67, and 93% of the possible yield of the carboline in two days at p_H 3·4, 4·6, 5·2, and 6·2, respectively. It is noteworthy that phenylpyruvic acid and its *m*-hydroxy-derivative condense most readily at two different values of p_H :



(XXXII.)

Percentage yield for p_H =	3·8	4·6	5·2	5·4	6·2	6·8
$Ph·CH_2·CO·CO_2H$ (13 days)	75	32	18	—	65	—
m-$OH·C_6H_4·CH_2·CO·CO_2H$ (8 days)	59	30	—	27	—	67

Sunlight causes the yield with the *m*-compound to rise to 87%, with time decrease to 4 days. All the above results relate to a condensation temperature of 25°. Increase of this to 37° is accompanied by decrease in yields.

G. Hahn and H. Werner[47] regard Scholz's conclusion[42] as invalid, in view of their work on the alkali scission of tetradehydroyohimbine. Of the two double bonds produced when lead tetra-acetate oxidises yohimbine, one must be at $C_5—C_6$, for it is unlikely that these two hydrogen atoms would first be removed by use of amyl-alcoholic alkali. The second double bond, according to these authors, will be at $C_{15}—C_{20}$. From the fact that C_{14} and C_{21} (in the alkali scission) appear as methyl groups, it follows at once that they cannot carry the hydroxyl group. In tetradehydroyohimbine, the ·CH(OH)· group is still present, and loses water first during the alkali scission. Were the Scholz formula correct, a double bond should appear at $C_{14}—C_3$ or at $C_{14}—C_{15}$, and then C_{14} could not appear as a methyl group. Hahn and Werner apply their synthetic methods to the question. They show that the 3-*m*-hydroxybenzyl-3 : 4 : 5 : 6-tetrahydronorharman (XXXIII) obtained by decarboxylating the product of one of the new condensation processes reacts almost instantaneously with formaldehyde at p_H 4·4 to give, in 88% yield, 3-(3′-hydroxy-6′-hydroxymethylbenzyl)-3 : 4 : 5 : 6-tetrahydronorharman hydrochloride (XXXIV), which when treated with alkali gives the hexadehydroyohimbol (XXXV). The analogous formaldehyde condensation in the plant would be likely to take place only if, as in (XXXIII), the hydroxyl group were in the meta-position to the benzyl methylene group, and it is therefore concluded that yohimbine itself is hydroxylated, not at C_{14} as supposed by Scholz, but at C_{17}.

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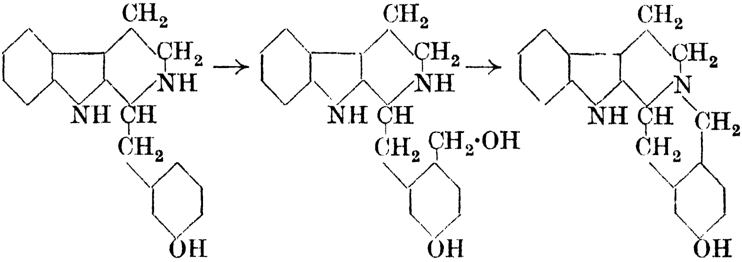
[46] *Annalen*, 1935, **520**, 107; *A.*, 1388.

[47] *Ibid.*, p. 123; *A.*, 1388.



(XXXIII.) (XXXIV.) (XXXV.)

Eserine (*Physostigmine*).—In view of the present confusion in the chemistry of eserine, the statement of the position by F. E. King and R. Robinson [48] is useful. One important piece of work is the optical resolution of *dl*-noreserethole [49] and the conversion of the active compound into metho-salts identical with those derived from eserine by successive hydrolysis, ethylation, and *N*-methylation. Some difficulty has arisen over the identity of a base, m. p. 80°, obtained by Hoshino and Kobayashi.[49] It is suggested by King and Robinson that it and their own *dl*-eserethole constitute a pair of stereoisomerides allied to those described by R. P. Linstead and E. M. Meade,[50] the fusion of two five-membered rings possibly permitting of this.

dl-Eserethole (XXXVIII) has now been synthesised [51] as follows, with good yields at all stages. *p*-α-Bromopropiono-*N*-methylphenetidide was converted by aluminium chloride into the hydroxy-compound (XXXVI), the ethyl ether of which was condensed with chloroacetonitrile in presence of sodium ethoxide. The other stages are reduction, condensation with benzaldehyde, treatment with methyl iodide, and reduction :

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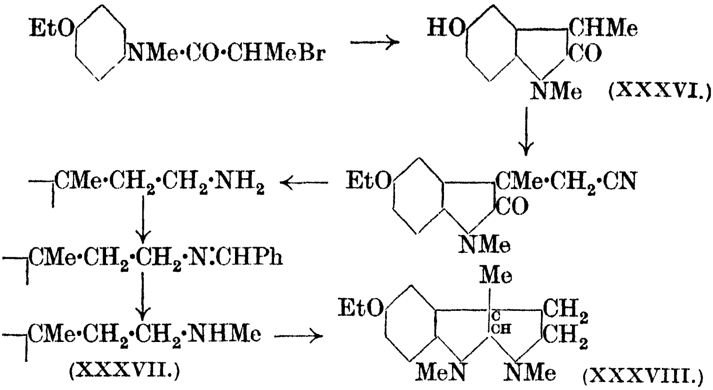
[48] *J.*, 1935, 755; *A.*, 925.

[49] T. Hoshino and T. Kobayashi, *Proc. Imp. Acad. Tokyo*, 1934, **10**, 564; *Annalen*, 1935, **516**, 81; *A.*, 227, 449.

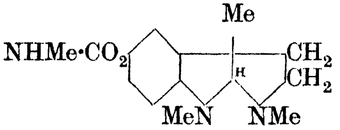
[50] *J.*, 1934, 935; *A.*, 1934, 1002.

[51] P. L. Julian and J. Pikl, *J. Amer. Chem. Soc.*, 1935, **57**, 563; *A.*, 635.

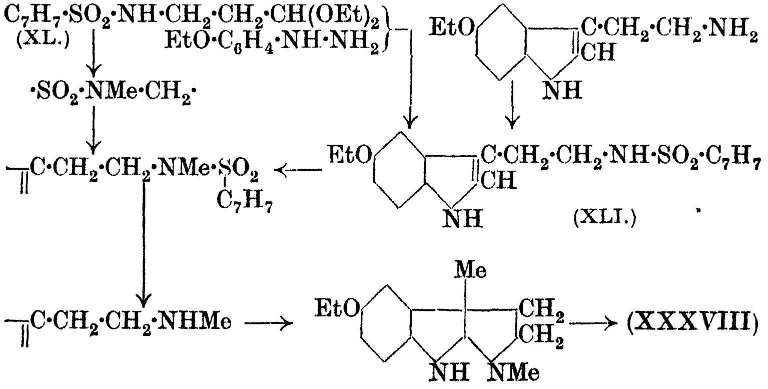


In a later paper, the same authors [52] record their failure to resolve *dl*-eserethole, but they resolved the intermediate compound (XXXVII) and, by reduction, obtained *l*-eserethole. When a petroleum solution of the last was warmed with aluminium chloride, *l*-eseroline was formed; so, since M. Polonovski and C. Nitzberg [53] had already converted *l*-eseroline into *l*-eserine (XXXIX), the complete synthesis of the latter has now been achieved.

(XXXIX.)



T. Hoshino and T. Kobayashi [54] have synthesised *dl*-eserethole in a different manner. *N*-*p*-Toluenesulphonyl-5-ethoxytryptamine



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[52] *J. Amer. Chem. Soc.*, 1935, **57**, 755; *A.*, 765.

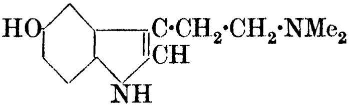
[53] *Bull. Soc. chim.*, 1916, [iv], **19**, 33; *A.*, 1916, i, 221.

[54] *Annalen*, 1935, **520**, 11; *A.*, 1378.

(XLI) was obtained either from 5-ethoxytryptamine and *p*-toluenesulphonyl chloride or by the action of alcoholic zinc chloride and *p*-ethoxyphenylhydrazine on γ-*p*-toluenesulphonamidobutaldehyde diethyl acetal (XL). Methylation then gave the *N*-methyl derivative, which was alternatively obtained from γ-*p*-toluenesulphonylmethylamidobutaldehyde diethyl acetal and *p*-ethoxyphenylhydrazine. Removal of the toluenesulphonyl group by the use of aniline and aniline hydrochloride gave 5-ethoxy-*N*-methyltryptamine, which, with ethylmagnesium iodide, followed by methyl iodide, gave *iso*noreserethole. The hydrochloride of this was converted by methyl iodide into *dl*-eserethole.

The same authors have also carried out the synthesis of bufotenine (XLII) from 5-ethoxyindole-3-acetonitrile, the $CH_2{\cdot}CN$ group being successively converted into $CH_2{\cdot}CO_2H$, $CH_2{\cdot}CO_2Et$, $CH_2{\cdot}CH_2{\cdot}OH$, $CH_2{\cdot}CH_2Br$, and $CH_2{\cdot}CH_2{\cdot}NMe_2$ by usual methods. The final product gave bufotenine when de-ethylated with aluminium chloride.

(XLII.)



Ergot Alkaloids.—Our knowledge of these alkaloids has increased considerably in the last few years. For an account of the older work, reference may be made to a paper by S. Smith and G. M. Timmis.[55] The work of Barger, Dale, Carr, and Kraft showed that ergotoxine and ergotinine were isomeric and interconvertible, boiling methyl alcohol changing ergotoxine into ergotinine, and hot dilute alcoholic phosphoric acid solution effecting the reverse change. A. Stoll [56] isolated a third alkaloid, ergotamine, which underwent isomeric change into a fourth alkaloid, ergotaminine, under conditions similar to those governing the ergotoxine–ergotinine conversions. This suggested a close relationship between ergotoxine and ergotamine, which was supported by the observation [57] that the physiological actions of these two bases were qualitatively and quantitatively identical; according to other authors,[58] ergotoxine had a biological activity 1·66 times that of ergotamine. Smith and Timmis, in the above paper, described the isolation of all four alkaloids in a state of high purity, and, by examining ergot from seven different European sources, they concluded that ergot of rye contains only ergotoxine and ergotinine, though a New Zealand ergot growing on *Festuca* contained ergotamine. In 1931,[59] they recorded the isolation of a new alkaloid, ψ-ergotinine, probably isomeric with ergotoxine.

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[55] *J.*, 1930, 1390; *A.*, 1930, 1050.

[56] *Schweiz. Apoth.-Ztg.*, 1922, **60**, 341; *A.*, 1923, i, 127; see also K. Spiro and A. Stoll, *Verh. Schweiz. Nat. Ges.*, 1920; *A.*, 1922, i, 47.

[57] H. H. Dale and K. Spiro, *Arch. exp. Path. Pharm.*, 1922, **95**, 337; *A.*, 1923, i, 420.

[58] E. Lozinski, G. W. Holden, and G. R. Diver, *J. Pharm. Exp. Ther.*, 1931, **42**, 123; *A.*, 1931, 871.

A. Soltys[60] showed that all four alkaloids on treatment with boiling alcoholic alkali gave one molecule of ammonia, and that oxidation of any of the alkaloids by permanganate and by nitric acid produced benzoic and *p*-nitrobenzoic acid, respectively.

Smith and Timmis,[61] following up this work, isolated a new, optically active base, ergine, $C_{16}H_{17}ON_3$, by heating any of the four alkaloids with alcoholic potassium hydroxide.

At this point, an outstanding series of papers by W. A. Jacobs began to appear. He found[62] that nitric acid oxidation of ergotinine gave also a tribasic acid, possibly $C_{14}H_9O_8N$, and, with L. C. Craig,[63] showed that ergotinine and methyl-alcoholic potassium hydroxide gave (1) an acid, $C_{14}H_{12}N(NMe)\cdot CO_2H$, named lysergic acid, (2) *iso*butyrylformic acid, and (3) ammonia, whereas, on similar treatment, ergine gave an acid which was at first thought not to be lysergic acid but was later identified as the acid sulphate of this substance. Smith and Timmis, however, showed[64] that ergine was the amide of an acid, $C_{15}H_{15}N_2\cdot CO_2H$, probably lysergic acid.

Jacobs and Craig found that lysergic acid was reducible with sodium and amyl alcohol to dihydrolysergic acid,[65] and that ergotinine,[66] when reduced with sodium and *n*-butyl alcohol, gave, in addition to one molecule of ammonia, seven products: (1) α-dihydrolysergol, $C_{16}H_{20}ON_2$, containing NMe and forming a monoacetyl derivative; (2) β-dihydrolysergol; (3) α-hydroxy*iso*valeric acid (formed from *iso*butyrylformic acid); and four bases, numbered II, IV, V, and VI. Since reduction of methyl lysergate gave (1) and (2) but none of the other products, it follows that the four bases arise from that part of the ergotinine molecule which is not lysergic acid, the two portions of the molecule possibly being joined by means of the *iso*butyrylformic acid skeleton. The formation of two dihydrolysergols is possibly due to the introduction of a new centre of asymmetry during the reduction of lysergic acid.

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[59] *J.*, 1931, 1888; *A.*, 1931, 1171.

[60] *Ber.*, 1932, **65**, [*B*], 553; *A.*, 1932, 629.

[61] *J.*, 1932, 763, 1543; *A.*, 1932, 526, 759.

[62] *J. Biol. Chem.*, 1932, **97**, 739; *A.*, 1932, 1147.

[63] *Ibid.*, 1934, **104**, 547; *A.*, 1934, 538.

[64] *Nature*, 1934, **133**, 579; *A.*, 1934, 667; *J.*, 1934, 674; *A.*, 1934, 787.

[65] *J. Biol. Chem.*, 1934, **106**, 393; *A.*, 1934, 1116.

[66] *Ibid.*, 1935, **108**, 595; *A.*, 504.

Later work [67] on the above four bases showed that base VI was a phenylpropanolamine, suggesting phenylalanine as its precursor in ergotinine. The same authors also identified, as a component of the above reduction mixture, proline methyl ester, which was also formed by the action of methyl-alcoholic hydrogen chloride on ergotinine. Bases II and IV were probably piperazine derivatives formed by reduction of prolylphenylalanine anhydride and proline anhydride respectively, and base V, probably α-pyrrolidylcarbinol, was derived from proline or its ester. This showed that ergotinine, and therefore ergotoxine, are built up of lysergic acid, $C_{16}H_{16}O_2N_2$ (or its amide, ergine, $C_{16}H_{17}ON_3$), proline, phenylalanine, and *iso*butyrylformic acid. Addition of these fragments with removal of four molecules of water gives $C_{35}H_{39}O_5N_5$, which is the empirical formula of ergotinine. At this point, Jacobs and Craig thought that lysergic acid, the pharmacologically important component of the alkaloids, was joined to a dipeptide composed of proline and phenylalanine.

These authors [68] also made a preliminary study of ergotamine. This was shown to give rise to lysergic acid, ammonia, and phenylalanine, but proline was not definitely identified. One important difference between ergotamine and ergotinine was discovered: none of the degradation processes used led to the formation of *iso*butyrylformic acid or of its reduction product, α-hydroxy*iso*valeric acid. Since in empirical formula the two alkaloids differ by C_2H_4, it was thought that in ergotamine (and ergotaminine) pyruvic acid might take the place of *iso*butyrylformic acid in ergotinine. Evidence for this was actually found.

G. Barger,[69] who, with A. J. Ewins,[70] first obtained *iso*butyrylformamide by the thermal decomposition of ergotoxine and ergotinine, obtained this amide, and ergine, from the ergoclavine described by W. Küssner.[71] Jacobs and Craig [72] found that ergotinine, when heated with hydrochloric acid, gave *l*-phenylalanine and proline methyl ester, whereas similar treatment of ergoclavine, alkaline hydrolysis of which gave ammonia, lysergic acid, and *iso*butyrylformic acid, gave *l*-leucine but no proline. Development [73] of the work on the alkaline hydrolysis of ergotinine [63] led to the isolation, in addition to lysergic acid and *iso*butyrylformic acid, of a mixture, acid hydrolysis of which gave almost inactive proline and phenyl-

[67] *J. Amer. Chem. Soc.*, 1935, **57**, 383; *A.*, 504.

[68] *Science*, 1935, **81**, 256; *A.*, 764.

[69] *Merck's Jahresber.*, 1933, **47**, 12.

[70] *J.*, 1910, **97**, 290.

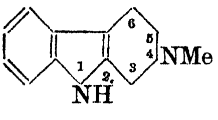
[71] *Merck's Jahresber.*, 1933, **47**, 5.

[72] *J. Amer. Chem. Soc.*, 1935, **57**, 960; *A.*, 872.

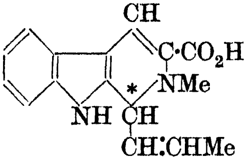
[73] *J. Biol. Chem.*, 1935, **110**, 521; *A.*, 1137.

alanine. Hydrolysis of ergotinine with hydrochloric acid, however, gave *l*-phenylalanine, what appeared to be a proline–phenylalanine dipeptide, and also *d*-proline methyl ester. Whilst, therefore, the phenylalanine has the usual configuration, that of the proline is unique in this instance, and, of course, a Walden inversion to explain it is probably out of the question. This confirmed the former conclusion that ergotinine and ergotoxine are composed of proline and phenylalanine combined in peptide linkage with lysergic acid, *iso*butyrylformic acid, and ammonia.

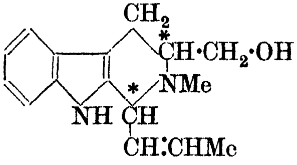
In their most recent paper,[74] Jacobs and Craig show that all the ergot alkaloids are derivatives of lysergic acid, in which the latter is conjugated with α-amino-acids or with substances derived from them. A return was made to dihydrolysergic acid, which was heated with potassium hydroxide at 300° in an atmosphere of hydrogen. The products were: (1) methylamine, (2) a substance which was probably 2-methyl-3-ethylindole, (3) propionic acid, and four other substances. It being known that by reduction with sodium and butyl or amyl alcohol lysergic acid gives a dihydro-derivative, and that ergotinine or methyl lysergate gives the corresponding alcohol (as α- and β-dihydrolysergols), and that it is difficult to reduce an indole structure, it becomes highly probable that at least one ethylenic linkage is present in another part of the molecule. This suggests a 4-carboline structure, and, since methylamine is formed almost quantitatively in the above decomposition, the basic carboline nitrogen atom probably carries the methyl group and is the salt-forming part of the molecule. This gives the partial structure (XLIII). To make up the 16 C of lysergic acid, there are also required a propyl or propylene side chain and a carboxyl group, these presumably being attached to the reduced ring. Further, the lysergic acid molecule has two double bonds.



(XLIII.)



(XLIV.)



(XLV.)

One is readily reduced and is probably at C_5—C_6 (compare harmine and harmaline giving tetrahydroharmine). The inferred relationship to tryptophan places the carboxyl at C_5, so lysergic acid would be (XLIV). This formula accounts for the optical activity, and explains the formation of the epimeric dihydrolysergols (XLV) from either ergotinine or methyl lysergate, since a new centre of asymmetry appears at C_5. The second double bond must be, as shown, in the side chain, but the latter may be an allyl group, undergoing the common bond-shift during alkali fusion. If both the carboxyl and the propenyl group are at C_3, it is more difficult to explain the epimeric dihydrolysergols. It may be observed that α-dihydrolysergol was shown to give a true onium salt with methyl iodide.

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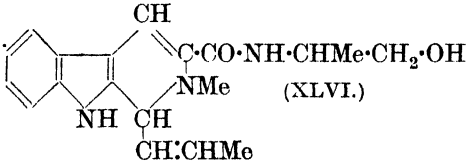
[74] *J. Biol. Chem.*, 1935, **111**, 455; *A.*, 1512.

A surprising new chapter in ergot chemistry was opened by H. W. Dudley and C. Moir,[75] who showed that the characteristic oxytocic effects of ergot were due, not to ergotoxine or to ergotamine, as had been thought, but to a new alkaloid, ergometrine, the extraction of which, by an improved method, was described by Dudley.[76] M. R. Thompson [77] also obtained evidence that there was a new alkaloid in ergot other than ergotoxine or ergotamine. Again, M. S. Kharasch and R. R. Legault [78] isolated " ergotocine " from ergot, and showed that under conditions (hot alkali) such as gave one molecule of ammonia with ergotoxine, ergotamine, and " sensibamine " (see below), no ammonia was formed. Lysergic acid was the only product identified. The " ergobasine," $C_{19}H_{23}O_2N_3$, isolated from ergot by A. Stoll and E. Burckhardt [79] was shown to be lysergic hydroxy*iso*propylamide.[80] M. R. Thompson [81] expressed the " belief " that ergostetrine (his new alkaloid) was identical with ergometrine, ergotocine, and ergobasine, and H. W. Dudley [82] put forward the same view more definitely.[83]


(XLVI.)

The validity of the arguments of Jacobs and Craig being assumed, the constitution of ergometrine is (XLVI). S. Smith and G. M.

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[75] *Brit. Med. J.*, 1935, i, 520; *A.*, 655.

[76] *Pharm. J.*, 1935, **134**, 709; *A.*, 894.

[77] *J. Amer. Pharm. Assoc.*, 1935, **24**, 24, 185; *A.*, 894.

[78] *J. Amer. Chem. Soc.*, 1935, **57**, 956, 1140; *A.*, 872, 995.

[79] *Compt. rend.*, 1935, **200**, 1680; *A.*, 995.

[80] W. A. Jacobs and L. C. Craig, *Science*, 1935, **82**, 16; *A.*, 1137.

[81] *J. Amer. Pharm. Assoc.*, 1935, **24**, 748; *A.*, 894.

[82] *Proc. Roy. Soc.*, 1935, [*B*], **118**, 478; *A.*, 1512.

[83] See also H. W. Dudley and C. Moir (*Science*, 1935, **81**, 559; *A.*, 1157); M. S. Kharasch and R. R. Legault (*ibid.*, p. 614; *A.*, 1157); M. R. Thompson (*ibid.*, p. 636; *ibid.*, **82**, 62; *A.*, 1157); N. L. Allport and S. K. Crews (*Quart. J. Pharm.*, 1935, **8**, 447; *A.*, 1512); and E. C. Kleiderer (*J. Amer. Chem. Soc.*, 1935, **57**, 2007; *A.*, 1512). As far as the writer is aware, the present account of ergot chemistry includes all references since 1930, up to December, 1935.

Timmis[84] have isolated yet another ergot alkaloid, ergometrinine, isomeric with, and convertible into, ergometrine, these two alkaloids being related in the same manner as ergotoxine–ergotinine and ergotamine–ergotaminine. The identity of ψ-ergotinine[59] remains unexplained.

It is possible now to summarise the present position as follows:

Active Alkaloids.	Inactive Alkaloids.	Components.	
Ergotoxine	Ergotinine	Lysergic acid	Ergine
$C_{35}H_{39}O_5N_5$		Ammonia	
		Proline	
		Phenylalanine	
		*iso*Butyrylformic acid	
Ergotamine	Ergotaminine	Lysergic acid	Ergine
$C_{33}H_{35}O_5N_5$		Ammonia	
		Proline ?	
		Phenylalanine	
		Pyruvic acid	
Ergometrine	Ergometrinine	Lysergic acid	
$C_{19}H_{23}O_2N_3$		β-Aminopropyl alcohol	
		(Hydroxy*iso*propylamine)	

The first four alkaloids give the same ergine, which is the amide of lysergic acid. Ergometrine, and presumably ergometrinine, give the same lysergic acid. It follows that the isomerism between the active and the inactive alkaloids must reside in the lysergic acid portion of the molecule. If the Jacobs–Craig formula for lysergic acid is correct, it would seem to follow that the isomerism must be due to *cis-* and *trans-*arrangements around the double bond in the side chain, although this is not altogether satisfactory, considering the conditions under which the isomeric changes occur.

(Sir) H. H. Dale pointed out[85] that the pharmacological activities of ergoclavine and sensibamine were identical with those of ergotoxine and ergotamine.[86] A. Stoll[87] showed that sensibamine was not a definite compound,[85] $C_{31}H_{37}O_5N_5$, but was a molecular compound, $C_{33}H_{35}O_5N_5$,$C_{33}H_{35}O_5N_5$, of ergotamine and ergotaminine. Ergoclavine is also probably a mixture, but it should be recalled that *l*-leucine was obtained by Jacobs and Craig[72] as one of its degradation products, and it is therefore possible that ergoclavine, which has been given the formula $C_{31}H_{37}O_5N_5$, is actually a mixture, one component of which is an undiscovered alkaloid, $C_{31}H_{37}O_3N_5$ or $C_{31}H_{35}O_2N_5$, built up from ergine, *l*-leucine, and phenylalanine.

Admitting that the constitution assigned to lysergic acid by Jacobs and Craig was not intended by them to be taken as final, it is not without interest to attempt to picture the possible structure of the alkaloids. The known chemistry of ergotoxine and ergotinine corresponds to a structure such as (XLVII) or (XLVIII).

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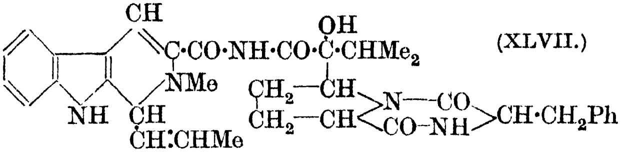
[84] *Nature*, 1935, **136**, 259; *A.*, 1256.

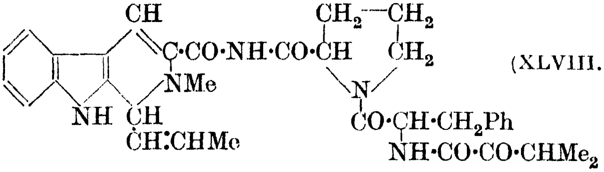
[85] *Schweiz. med. Woch.*, 1935, **65**, 885.

[86] A. Vartiainen, *J. Pharm. Exp. Ther.*, 1935, **54**, 259.

[87] *Schweiz. med. Woch.*, 1935, **65**, 1077.



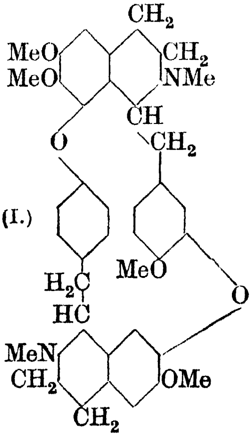
(XLVII.)



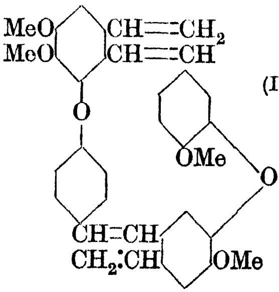
(XLVIII.)

In ergotamine and ergotaminine, the group $CO{\cdot}CO{\cdot}CHMe_2$ would be replaced by $CO{\cdot}CO{\cdot}CH_3$ (XLVIII); in (XLVII) $CO{\cdot}C(OH){\cdot}CHMe_2$ would be replaced by $\cdot CO{\cdot}C(OH)Me$.

Curare Alkaloids (*South American Arrow Poisons*).—An investigation of more than usual interest is that of the curare alkaloids by H. King,[88] who has obtained Boehm's tubocurarine in a crystalline condition, and submitted it to degradation processes. Curine, the crystalline alkaloid accompanying tubocurarine, was



(I.)



(II.)

shown by E. Späth, W. Leithe, and F. Ladeck [89] to be the lævo-modification of *d*-bebeerine. H. King[90] suggested a probable formula for curine, which was supported by the experimental work of E. Späth and F. Kuffner,[91] who assigned to *O*-methylcurine the structure (I). King has now [92] carried out the exhaustive methylation of the accessible base, *d*-curine (*d*-bebeerine), obtaining in this way the known *O*-methylbebeerine methochloride. Hofmann degradation of the latter gave three distinct methine bases, and thence three crystalline methiodides. Hofmann degradation of the mixture of the three methochlorides gave trimethylamine and a substance, $C_{36}H_{32}O_6$. Similar degradation of *d*-*O*-methyltubocurarine chloride led to a mixture of four methine methiodides, three of which were identical with the above three methiodides, the fourth being *l*-*O*-methyltubocurarinemethine methiodide. The second degradation stage gave trimethylamine and the substance $C_{36}H_{32}O_6$. If *O*-methylbebeerine is regarded as (I), the latter substance can be accounted for as (II). It is probable, however, that although *O*-methylbebeerine methochloride and *O*-methyltubocurarine methochloride are diastereoisomerides, the parent phenolic substances, bebeerine methochloride and tubocurarine methochloride, have different arrangements of hydroxyl and methoxyl groups.

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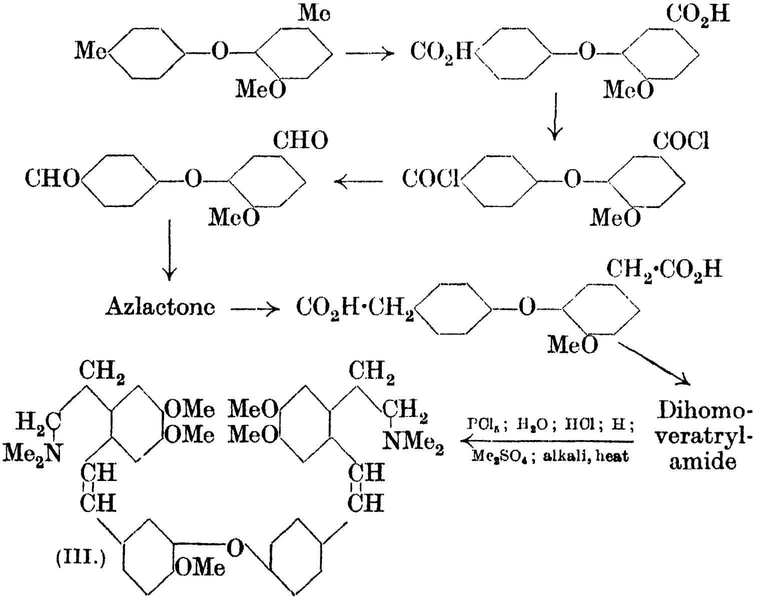
[88] *Chem. and Ind.*, 1935, 739; *A.*, 1138.

[89] *Ber.*, 1928, **61**, [*B*], 1705; *A.*, 1928, 1264.

[90] *Ann. Reports*, 1933, **30**, 249.

Dauricine.—The constitution of this alkaloid has been proved [93] by a synthetic method, methyldauricine-α-methine (III) being obtained as follows :



(III.)

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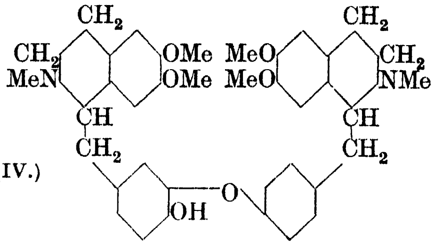
[91] *Ber.*, 1934, **67**, [*B*], 55; *A.*, 1934, 312. [92] *J.*, 1935, 1381.

[93] H. Kondo, Z. Narita, and S. Uyeo, *Ber.*, 1935, **68**, [*B*], 519; *A.*, 637.

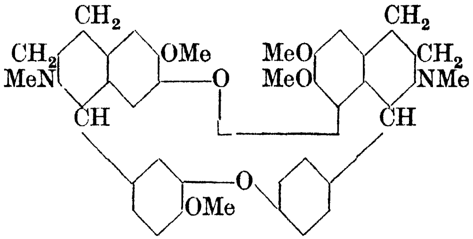
From this it follows that dauricine has the constitution (IV) suggested by F. Faltis and H. Frauendorfer.[94]

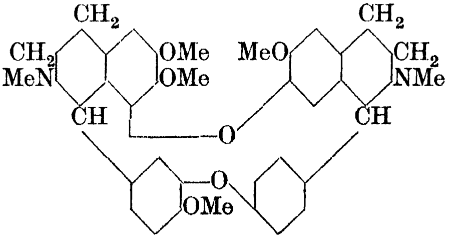


(IV.)

Phaeanthine.—Whereas A. C. Santos[95] found this alkaloid to be $C_{37}H_{38}O_6N_2$, H. Kondo and I. Keimatsu[96] find it to be $C_{38}H_{42}O_6N_2$, and a comparison of its physical properties with those of tetrandrine suggested that these two alkaloids are optical antipodes. The absorption curves support this view.[97] Probably tetrandrine, *iso*tetrandrine, and phaeanthine represent three out of the four possible stereoisomerides corresponding to the two asymmetric carbon atoms in (V) and (VI), which are the two possible structural formulæ for the alkaloids :[98]

(V.)





(VI.)

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[94] *Ber.*, 1930, **63**, [*B*], 809; *A.*, 1930, 774.

[95] *Ber.*, 1932, **65**, [*B*], 472; *A.*, 1932, 527.

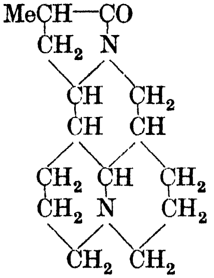
[96] *Ber.*, 1935, **68**, [*B*], 1503.

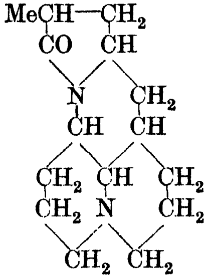
[97] H. Kondo and I. Keimatsu, *J. Pharm. Soc. Japan*, 1935, **636**.

[98] F. von Bruchhausen, H. Oberembt, and A. Feldhaus, *Annalen*, 1933, **507**, 144; *A.*, 1933, 1313.

Sophora Alkaloid.—H. Kondo, E. Ochiai, and K. Tsuda[99] have almost completed their investigation of the constitution of matrine, one of the principal alkaloids in the roots of *Sophora flavescens*. The alkaloid, which is not a stereoisomeride of lupanine, is probably either (VII) or (VIII).

(VII.)

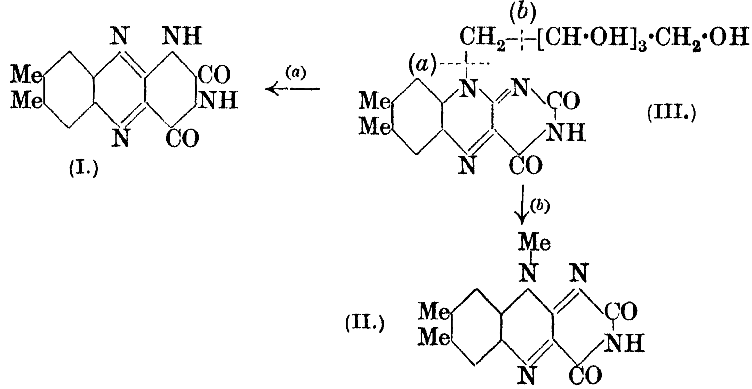




(VIII.)

Lactoflavin.

Last year, R. Kuhn, R. Reinemund, and F. Weygand[1] described the synthesis of lumilactoflavin (II) by a modification of the Kühling condensation. P. Karrer, H. Salomon, K. Schöpp, E. Schlittler, and H. Fritzsche[2] showed that, if lactoflavin (vitamin-B_2) is irradiated, not in strongly alkaline solution (when lumilactoflavin is produced), but in dilute methyl-alcoholic solution, lumichrome (I) (6 : 7-dimethylalloxazine) is formed, and they suggested that lactoflavin probably contained a pentose chain, $CH_2 \cdot C_4H_9O_4$, in position 9. In a later paper[3] the two decompositions induced by irradiation were pictured thus :



(I.) (III.) (II.)

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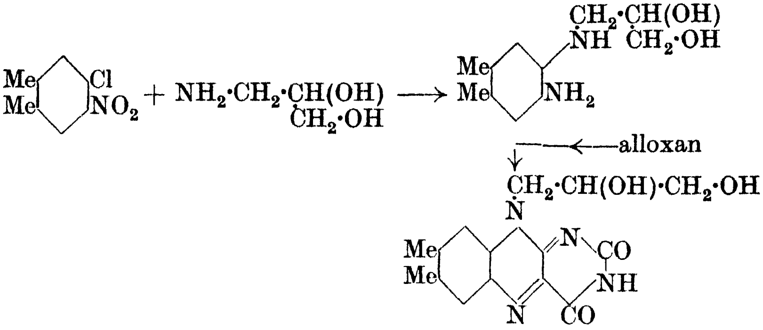
[99] *Ber.*, 1935, **68**, [*B*], 1899; *A.*, 1514. Parts I to IV and XV to XVII of Kondo's papers on matrine may be found in *A* abstracts. The rest have not been abstracted.

[1] *Ber.*, 1934, **67**, [*B*], 1460; *A.*, 1934, 1114.

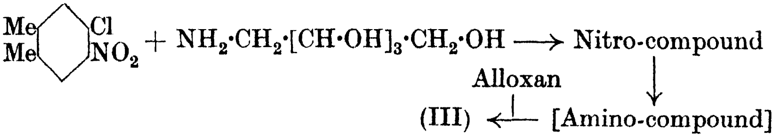
[2] *Helv. Chim. Acta*, 1934, **17**, 1010; *A.*, 1934, 1233.

[3] P. Karrer, H. Salomon, K. Schöpp, and E. Schlittler, *ibid.*, p. 1165; *A.*, 1934, 1233.

and the following synthesis of an analogous but less complex substance was described :



Since the simpler product closely resembled lactoflavin, the above constitution (III) for the latter was supported. At approximately the same time, R. Kuhn and F. Weygand,[4] starting with *l*-arabinose and *d*-xylose, synthesised in the following manner, two compounds (III), both of which resembled lactoflavin in solubility, absorption spectrum, and dependence of fluorescence on p_H, formed a red radical when reduced in mineral acid solution, and gave lumilactoflavin when irradiated in alkaline solution :



P. Karrer and K. Schöpp, who had already [5] described the isolation of a flavin from green malt, later showed [6] that irradiation of crystallised ovoflavin-*e* from dry technical ovalbumin gave 6 : 7-dimethylalloxazine. R. Kuhn and F. Weygand [7] pointed out that there were eight possible stereoisomerides corresponding to formula (III) above, and expressed the view that lactoflavin was most probably the *l*-arabo- or the *d*-ribo-compound [8] (III). The same authors [9] had previously stated that the *l*-arabo-compound had the same growth-promoting effect as natural lactoflavin, at the same time showing that the corresponding compound devoid of the two methyl groups in one nucleus was inactive in that respect.

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[4] *Ber.*, 1934, **67**, [*B*], 1939; *A.*, 1935, 224.

[5] *Helv. Chim. Acta*, 1934, **17**, 1013; *A.*, 1934, 1233.

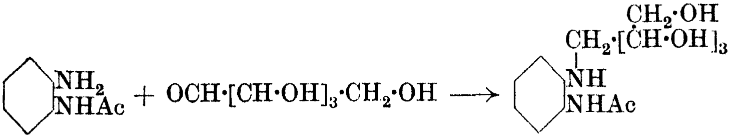
[6] *Ibid.*, p. 1557; *A.*, 1935, 95.

[7] *Ber.*, 1935, **68**, [*B*], 166; *A.*, 358.

[8] Compare R. Kuhn and H. Rudy, *ibid.*, p. 169; *A.*, 359,

[9] *Ber.*, 1934, **67**, [*B*], 2084; *A.*, 1935, 262.

A different type of synthesis was introduced by P. Karrer, K. Schöpp, F. Benz, and K. Pfaehler,[10] who found that, whereas the condensation of *o*-chloronitrobenzenes with amino-sugars was not particularly satisfactory, good results in the preliminary stages were obtained by the reductive condensation of the monoacetyl derivative of *o*-phenylenediamines with aldoses :



By this method, these authors synthesised Kuhn's *l*-arabo-compound (III), and they too thought that the latter might be identical with natural lactoflavin, the observed differences possibly being due to impurities in the natural product.

At this stage, R. Kuhn and H. Kaltschmitt[11] showed that the lactoflavin isolable as the tetra-acetyl derivative from Californian lucerne was identical with milk lactoflavin. It may be noted that, according to L. J. Harris,[12] Kuhn's lactoflavin had no anti-pellagra action, and in this view he was supported by P. György.[13] Yet B. C. P. Jansen[14] regarded the identity of lactoflavin and vitamin-B_2 as established.

Shortly after this, P. Karrer, K. Schöpp, and F. Benz[15] described the synthesis of two compounds of formula (III), one being the *d*-xylo-compound obtained by Kuhn and Weygand,[4] the other a new substance, 6 : 7-dimethyl-9-*d*-1′-ribityl*iso*alloxazine (III; IV), which resembled natural lactoflavin extremely closely, the tetra-acetyl derivatives also being very similar. In a paper sent in five days later than that by Karrer and his co-workers, R. Kuhn, H. Rudy, and F. Weygand[16] definitely expressed the opinion that 6 : 7-dimethyl-9-*l*-araboflavin could not be identical with lactoflavin, since it was at least three times less effective than the latter in growth-promoting activity. These authors further said that lactoflavin was possibly the *d*-ribo-compound (III; IV), and announced a new type of synthesis of the *d*-arabo-compound, starting from 4 : 5-dinitro-*o*-xylene :

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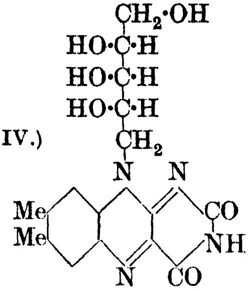
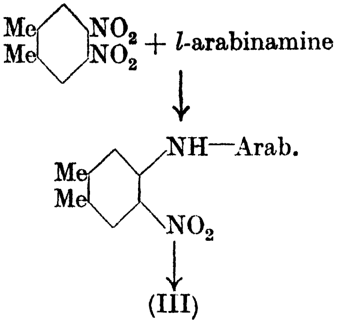
[10] *Ber.*, 1935, **68**, [*B*], 216; *A.*, 359.
[11] *Ibid.*, p. 128; *A.*, 415.
[12] *Biochem. J.*, 1935, **29**, 776; *A.*, 545.
[13] *Ibid.*, p. 741; *A.*, 545.
[14] *Nature*, 1935, **135**, 267; *A.*, 545.
[15] *Helv. Chim. Acta*, 1935, **18**, 426; *A.*, 631.
[16] *Ber.*, 1935, **68**, [*B*], 625; *A.*, 760.



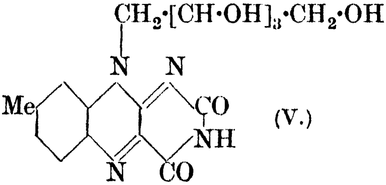
(IV.)



6 : 7-Dimethyl-9-*l*-araboflavin (Kuhn) = 6 : 7-Dimethyl-9-*l*-1′-arabityl*iso*alloxazine (Karrer).

Other workers[17] confirmed the identity of the riboflavin with lactoflavin, and showed that most other synthetic flavins (xylityl, rhamnityl, sorbityl, dulcityl, and mannityl) had no biological activity, although the *l*-araboflavin had some. They also pointed out that lactoflavin is the growth-promoting substance present in vitamin-B_2, but is not necessarily the anti-pellagra factor, and this would explain the results of C. A. Elvehjem and C. J. Koehn.[18] At the same time, Karrer and his co-workers[17] described the reductive condensation of *d*-ribose with the mono-urethane derived from 4 : 5-diamino-*o*-xylene as an alternative first stage in the flavin synthesis.

In order further to remove doubt as to the identity of lactoflavin, the antipodal varieties of *d*-ribo- and *l*-arabo-flavins were prepared.[19] It was found that *l*-riboflavin had no growth-promoting action. An interesting point was also discovered by the same authors,



(V.)

namely, that 7-methyl-9-*d*-1′-ribityl*iso*alloxazine (V) had strong vitamin-B_2 action; the *o*-xylene structure, therefore, is not essential for the latter. Later[20] they described the synthesis of the eighth and last possible compound of structure (III), *viz.*, 6 : 7-dimethyl-9-*d*-1′-lyxityl*iso*alloxazine, this establishing finally the configuration of the sugar residue in lactoflavin. Examination[21] of the fluorescence spectra of several synthetic flavins further confirmed the same point.

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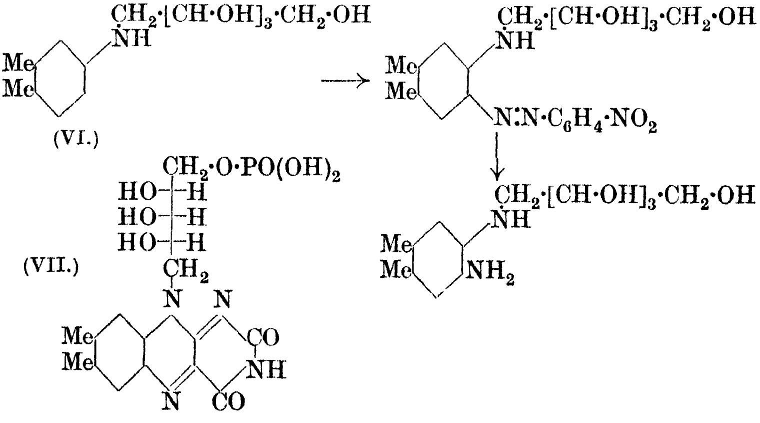
[17] H. von Euler, P. Karrer, M. Malmberg, K. Schöpp, F. Benz, B. Becker, and P. Frei, *Helv. Chim. Acta*, 1935, **18**, 522; *A.*, 760. See also P. Karrer, H. von Euler, M. Malmberg, K. Schöpp, and F. Benz, *Svensk Kem. Tidskr.*, 1935, **47**, 99; *A.*, 1286.

[18] *J. Biol. Chem.*, 1935, **108**, 709; *A.*, 669.

[19] P. Karrer, H. Salomon, K. Schöpp, F. Benz, and B. Becker, *Helv. Chim. Acta*, 1935, **18**, 908; *A.*, 1134.

R. Kuhn and F. Weygand[22] found that the yield of flavins obtained by condensing sugar derivatives of *o*-diamines with alloxan is enormously improved if boric acid is used instead of hydrochloric acid as the condensing agent, moderately anhydrous solvents being beneficial. For instance, when the *N*-arabityl derivative of diaminoxylene was treated with zinc dust and boric acid in boiling glacial acetic acid, followed by addition of alloxan, a 52% yield of the flavin was formed. Even with 2-aminodiphenylamine and alloxan under these conditions a 63% yield of 9-phenyl*iso*alloxazine may be obtained.

Another interesting flavin synthesis is due to P. Karrer and H. F. Meerwein.[23] *o*-4-Xylidine was reductively condensed with *d*-ribose in presence of nickel or palladium, the product (VI) coupled with diazotised *p*-nitroaniline, the azo-derivative catalytically reduced under high pressure in presence of nickel, and the resulting base condensed with alloxan :


(VI.)

(VII.)

In a summary of their work, Kuhn and his collaborators[24] stress the advantages of their synthetic methods, particularly (1) the use of palladium and not nickel for reductive condensations (Karrer's method necessitating the employment of high pressures), and (2) the use of boric acid in the final stage, yields of 90% being recorded with *d*-riboflavin : condensation of *N*-*d*-ribityldiaminoxylene with alloxan was carried out in glacial acetic acid solution at the ordinary temperature.

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[20] P. Karrer, H. Salomon, K. Schöpp, and F. Benz, *Naturwiss.*, 1935, **23**, 355; *A.*, 993.

[21] P. Karrer and H. Fritzsche, *Helv. Chim. Acta*, 1935, **18**, 911; *A.*, 1134.

[22] *Ber.*, 1935, **68**, [*B*], 1282; *A.*, 1134.

[23] *Helv. Chim. Acta*, 1935, **18**, 1130; *A.*, 1510.

[24] R. Kuhn, K. Reinemund, F. Weygand, and R. Ströbele, *Ber.*, 1935, **68**, [*B*], 1765; *A.*, 1382.

An account of some of the work on lactoflavin was given in a lecture by R. Kuhn.[25] In this it is suggested that the parent yellow plant enzyme corresponding to lactoflavin is (VII). This acid, in the form of its sodium salt, was prepared[26] by treating lactoflavin with phosphoryl chloride in presence of pyridine.

E. E. T.

8. The Porphyrin Group.[1]

General.

Great advances have been made during the last few years in the chemistry of this group, which constitutes probably the most important class of natural organic colouring matters and is of the greatest biological interest.[2] Developments in the study of hæmin and associated compounds have already been reported.[3] The chemistry of chlorophyll is reviewed below, together with that of other natural porphyrins.

The biological importance of the porphyrins tends to obscure their great chemical interest. Before considering in detail the natural pigments, we may briefly examine the peculiarity of the common structural unit. It is now generally believed that the porphyrins contain the basic unit porphin (A),[4] as was first proposed by W. Küster for the blood pigment. The synthesis of this parent substance in very poor yield was achieved by Hans Fischer, after much negative work,[5] by heating pyrrole-2-aldehyde with alcohol in boiling formic acid. The substance is a typical porphyrin in its general properties, notably in its spectrum. The free compound has a five-banded spectrum with two sharp bands in the green region ; the copper compound has the usual two-banded spectrum of the metallic porphyrins, and the iron compound gives a typical hæmochromogen spectrum on treatment with hydrazine. Simple derivatives such as octamethylporphin[6] (with methyl groups on the β-positions of the pyrrole rings) have been known for some time.

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[25] *Bull. Soc. Chim. biol.*, 1935, **17**, 905.

[26] R. Kuhn and H. Rudy, *Ber.*, 1935, **68**, [*B*], 383 ; *A.*, 545.

[1] The term should be read to include the free porphyrins, their metallic derivatives, and substances of similar cyclic structure.

[2] A. Treibs's recent discoveries of porphyrins in petroleum and coal have given the group a geochemical significance also (see p. 398).

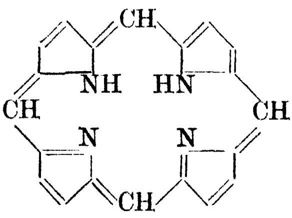
[3] *Ann. Reports*, 1932, **29**, 209.

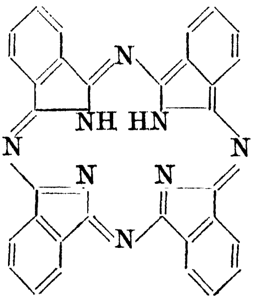
[4] F. Haurowitz and his associates have proposed a free-radical variant of this (*Ber.*, 1935, **68**, [*B*], 1795 ; *A.*, 1384).

[5] H. Fischer and W. Gluin, *Annalen*, 1935, **521**, 157.

The Küster formula was not at first accepted, for, as Willstätter pointed out, it contained a 16-membered ring of a type without parallel. The evidence in its support comes mainly from the synthetic work of H. Fischer.[7] The syntheses of porphyrins by the condensation of 3 : 4-dialkylpyrroles (such as opsopyrrole), with formaldehyde or formic acid,[8] and by the fusion of 2 : 2′-dibromodipyrrylmethenes with 2 : 2′-dimethyldipyrrylmethenes in succinic acid,[9] are of particular value as indicating the structure.

(A)





(B)

[The positions of the imino-hydrogen atoms and the double bonds in these formulæ are arbitrary.]

All these synthetic methods, however, involve a loss of hydrogen in the final condensation, apart from the hydrogen bromide or water, etc., eliminated between the condensing groups, and none provides a final proof of structure; nor, from the very complexity of the molecule, is this to be expected. On the other hand, the cumulative evidence is very strong, and the Küster formula not only accounts for all the reactions of porphyrins, but also provides a satisfactory basis for Fischer's important investigations of their isomerism.[3]

The recently discovered phthalocyanines[10] throw some light on the problem. The formula (B) given to phthalocyanine on chemical evidence[11] has been confirmed by J. M. Robertson's *X*-ray examination.[12] The molecular weight[13] and the dimensions[12] have been determined and the structure is certain (apart from detail of the fine structure). The entry of a metallic atom has hardly any effect on the size of the molecule.[12] Phthalocyanine contains a central 16-membered ring of a type essentially similar to that postulated for the porphyrins (but containing 4 —N= for 4 —CH=) and resembles the latter in many physical and chemical properties.[11] There is no doubt, therefore, that stable rings of this type can exist and the Küster formula is strongly supported by the resemblance.[14]

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[6] H. Fischer and B. Walach, *Annalen*, 1926, **450**, 164; *A.*, 1926, 1261.

[7] H. Fischer and co-workers, *ibid.*, 1926, **448**, 178, 193, etc.; *A.*, 1926, 962, 963; particularly 1928, **462**, 240; *A.*, 1928, 902. Cf. *Ann. Reports*, 1932, **29**, 209.

[8] H. Fischer and A. Treibs, *Annalen*, 1926, **450**, 132; *A.*, 1926, 1256; *Ber.*, 1927, **60**, 379; *A.*, 1927, 365.

[9] H. Fischer, P. Halbig, and B. Walach, *Annalen*, 1927, **452**, 268; *A.*, 1927, 469.

[10] R. P. Linstead, *J.*, 1934, 1016; *A.*, 1934, 1114.

When these large rings are present the chemistry of the molecule is profoundly modified; *e.g.*, phthalocyanine shows none of the ordinary instability of an *iso*indole derivative, nor a porphyrin that of a pyrrole. There is in fact an approach to an aromatic character, presumably arising from the formation of the unbroken conjugated ring. This is seen in the tendency to formation and in the great stability of the type. The porphyrin nucleus survives the most diverse chemical treatment. Unlike almost all other coloured organic compounds, porphyrins are not reduced by alkaline hyposulphite or by hydrogen over palladium in alkaline solution.[15] They are reduced by more drastic reagents, but are readily regenerated from the leuco-compounds (Fischer, R. Kuhn, Conant). Porphyrins can be halogenated,[16,17] nitrated,[17,18] and sulphonated.[19] The stereochemistry of both phthalocyanine and the porphyrins is essentially aromatic; the phthalocyanine ring has been proved experimentally to be flat[12] and porphyrins show no optical activity.[20]

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[11] C. E. Dent, R. P. Linstead, and A. R. Lowe, *J.*, 1934, 1033; *A.*, 1934, 1114.

[12] *J.*, 1935, 615; *A.*, 813. F. Haurowitz (ref. 4) has also found that metallic derivatives of porphyrins have substantially the same dimensions as the parent substances.

[13] J. M. Robertson, R. P. Linstead, and C. E. Dent, *Nature*, 1935, **134**, 506; *A.*, 689; cf. R. P. Linstead and A. R. Lowe, *J.*, 1934, 1031; *A.*, 1934, 1114.

[14] In the last few months, H. Fischer, H. Haberland, and A. Müller (*Annalen*, 1935, **521**, 122) have described pyrrole derivatives of a new type, called di-iminoporphyrins. These contain four pyrrole rings joined on two sides by the ordinary methenes and on the other two sides by (—NH—) or (—N=) groups. These substances to some extent bridge the gap between porphyrins and phthalocyanines.

[15] J. B. Conant and J. F. Hyde, *J. Amer. Chem. Soc.*, 1930, **52**, 1233; *A.*, 1930, 799.

[16] H. Fischer and G. Stangler, *Annalen*, 1927, **459**, 53; *A.*, 1928, 76.

[17] H. Fischer and W. Neumann, *ibid.*, 1932, **494**, 228; *A.*, 1932, 626.

[18] H. Fischer, M. Speitman, and H. Meth, *ibid.*, 1934, **508**, 154; *A.*, 1934, 308.

[19] A. Treibs, *ibid.*, 1933, **506**, 196; *A.*, 1933, 1309.

[20] H. Fischer and A. Stern, *ibid.*, 1935, **519**, 58; **520**, 88; *A.*, 1135, 1383.

The absorption spectra of porphyrins in the visible region are remarkably like the ultra-violet spectrum of benzene.[21] Finally, no isomerides are known corresponding with changes in the fine structure; *e.g.*, no porphyrin exists in two forms, one with the imino-hydrogen atoms on adjacent pyrrole rings (as in A), the other with them on diagonally opposite rings. Neither are isomeric metallic derivatives of these forms known (Fischer, Conant, Dietz). The same appears to be true of phthalocyanines. This of course corresponds with the fact that *o*-disubstituted benzenes do not exist in two forms.

Chlorophyll.[22]

Chlorophyll has occupied the attention of chemists for nearly a century, since Berzelius first attempted to isolate the pigment from green leaves, but it is only in the last thirty years that real progress has been made. To-day the problem of its constitution is nearly solved, thanks mainly to the researches of Willstätter and Hans Fischer and their collaborators. Valuable contributions have also been made by J. B. Conant, A. Stoll, and L. Marchlewski. Some of the earlier work has already been summarised in these Reports,[23] but a short critical review of it in the light of the most recent developments is now given because the problem and the nomenclature are very complex and the early results have been corrected in some respects.

Chlorophyll occurs in the chloroplasts of green plants, mainly in the leaves, accompanied by the yellow pigments carotin, xanthophyll, and (in brown algæ) fucoxanthin. G. G. Stokes[24] and H. C. Sorby[25] provided the first evidence that chlorophyll is not homogeneous and this was confirmed by M. Tswett,[26] the discoverer of the chromatographic method of analysis. At one time it was thought that a large number of different chlorophylls existed, that of monocotyledons, for example, being different from that of dicotyledons, but this was disproved by R. Willstätter,[27] who showed that chlorophyll from a wide variety of sources is a mixture of two very similar pigments, the blue-green chlorophyll *a* and the yellow-green chlorophyll *b*. The proportion of these forms in land plants is about 3 of *a* to 1 of *b*, but the amount of *b* is much smaller in brown algæ. Dry leaves contain some 0·8% of mixed chlorophylls. One recent claim [28] for the discovery of a third form (*c*) has been disproved,[29] but an independent line of evidence, although indirect, suggests that chlorophyll *a* may itself be a mixture of two isomerides.[30]

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[21] J. B. Conant and S. E. Kamerling, *J. Amer. Chem. Soc.*, 1931, **53**, 3522; *A.*, 1931, 1310; see p. 390.

[22] General accounts are given by R. Willstätter and A. Stoll ("Untersuchungen über Chlorophyll," Berlin, 1913) and by H. Fischer (Oppenheimer's "Handbuch der Biochemie," 1923, 351; 1930, 87; 1933, 262; *J.*, 1934, 245), and valuable short reviews by K. F. Armstrong (*Chem. and Ind.*, 1933, 809) and E. M. Dietz (*J. Chem. Educ.*, 1935, **12**, 208).

[23] *Ann. Reports*, 1911, **8**, 144; 1912, **9**, 169; 1913, **10**, 151.

[24] *Proc. Roy. Soc.*, 1864, **13**, 144; *J.*, 1864, **17**, 304.

[25] *Proc. Roy. Soc.*, 1873, **21**, 442.

[26] *Ber.*, 1908, **41**, 1352; *Ber. deut. bot. Ges.*, 1906, **24**, 316; *A.*, 1908, i, 440; 1906, i, 973.

[27] R. Willstätter and A. Stoll, "Chlorophyll," p. 117.

Chlorophyll is a waxy solid which has not yet been obtained crystalline. When green leaves are extracted with alcohol, a crystalline green pigment is produced,[31] but this involves a secondary decomposition, the formation of a chlorophyllide. Chlorophyll is best isolated by extracting dried green leaves with acetone containing 15—20% of water; the solution is then diluted with light petroleum, and the acetone removed with water.[32] About 80% of the total chlorophyll can be extracted in this way. Tswett [26] separated crude chlorophyll in small amounts into the *a* and the *b* component (and the carotenoids) by passing a benzene solution through a column of calcium carbonate or sugar. R. Willstätter and M. Isler removed the chlorophyll *b* by extracting the petroleum solution of the crude pigment with 90% methyl alcohol.[33] Tswett's method has been improved by A. Winterstein and G. Stein,[34] and Willstätter's by A. Stoll and E. Wiedemann.[35] Absorption spectra indicate that the older preparations of chlorophyll *b* contained some 10% of *a*. For work on the degradation products it is usual, not to separate the two chlorophylls, but to hydrolyse the mixed pigment to phæophorbide (*a* + *b*) and separate this into its components by acid fractionation (p. 366).

Chlorophyll and closely related substances retain solvents (particularly water) tenaciously and their analysis is difficult. The formulæ originally given to the two components by Willstätter,[36] and accepted to-day, are: *a*, $C_{55}H_{72}O_5N_4Mg$; *b*, $C_{55}H_{70}O_6N_4Mg$.

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[28] F. P. Zscheile, *Bot. Gaz.*, 1934, **95,** 529; *A.*, 1934, 1115.

[29] A. Winterstein and K. Schön, *Z. physiol. Chem.*, 1934, **230,** 139; *A.*, 1935, 362.

[30] J. B. Conant and E. M. Dietz, *Nature*, 1933, **131,** 131; *A.*, 1933, 287; see p. 388.

[31] J. Borodin, *Bot. Ztg.*, 1882, **40,** 608.

[32] R. Willstätter and E. Hug, *Annalen*, 1910, **378,** 21; *A.*, 1911, i, 393.

[33] *Ibid.*, 1912, **390,** 269; *A.*, 1912, i, 710.

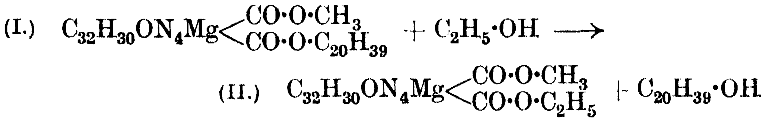
[34] *Z. physiol. Chem.*, 1933, **220,** 263; *A.*, 1934, 91; compare ref. 29.

[35] *Helv. Chim. Acta*, 1933, **16,** 739; *A.*, 1933, 838.

[36] "Chlorophyll," p. 144. The analyses for chlorophyll *a* actually agreed with the values required for a semihydrate, $C_{55}H_{72}O_5N_4Mg,\frac{1}{2}H_2O$.

Earlier workers had believed that chlorophyll contained iron, phosphorus, and other elements. The quantitative basis for these formulæ is mainly the analysis of degradation products, particularly the chlorophyllides and phæophorbides.

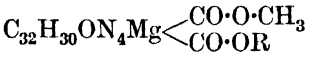
Chlorophyllides.—Willstätter found that, when chlorophyll in green leaves is extracted with ethyl alcohol, a phytyl group ($C_{20}H_{39}$) is replaced by ethyl, the reaction being catalysed by an enzyme, chlorophyllase, present in the leaf.[37] The bluish-green product ("crystalline chlorophyll") is a mixture of ethyl chlorophyllides ($a + b$), which form mixed crystals. These may be separated by partition between aqueous methyl alcohol and a mixture of ether and light petroleum. Ethyl chlorophyllide a has the formula $C_{37}H_{38}O_5N_4Mg$ and the change in the a series is interpreted by Willstätter as follows:



$$\text{(I.)}\quad C_{32}H_{30}ON_4Mg\Big<\begin{matrix}CO\cdot O\cdot CH_3\\ CO\cdot O\cdot C_{20}H_{39}\end{matrix} + C_2H_5\cdot OH \longrightarrow$$

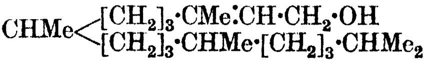
$$\text{(II.)}\quad C_{32}H_{30}ON_4Mg\Big<\begin{matrix}CO\cdot O\cdot CH_3\\ CO\cdot O\cdot C_2H_5\end{matrix} + C_{20}H_{39}\cdot OH$$

These formulæ embody the fact (proved later) that chlorophyll and ethyl chlorophyllide contain a carbomethoxy-group. This made the examination of the structure of ethyl chlorophyllide difficult, because Zeisel determinations yielded a mixture of methyl and ethyl iodides. Methyl chlorophyllide a (III, $R = CH_3$) can be made similarly, and a free chlorophyllide a (III, $R = H$) by hydrolysing leaf chlorophyll with acetone containing 33% of water and separating the a and the b component by partition.[38]



$$C_{32}H_{30}ON_4Mg\Big<\begin{matrix}CO\cdot O\cdot CH_3\\ CO\cdot OR\end{matrix}$$

(III.)



$$CHMe\Big<\begin{matrix}[CH_2]_3\cdot CMe{:}CH\cdot CH_2\cdot OH\\ [CH_2]_3\cdot CHMe\cdot[CH_2]_3\cdot CHMe_2\end{matrix}$$

(IV.)

In the chlorophyllase reaction the phytyl group is liberated as phytyl alcohol (IV), the structure of which has been determined by F. Gottwalt Fischer and K. Löwenberg,[39] who synthesised it from ψ-ionone. It contains four isoprene units. The chlorophyll from about 200 different plants yields the same phytol in some 30% yield.[40] The phytyl group is responsible for the wax-like properties of chlorophyll and its power of forming colloidal solutions.

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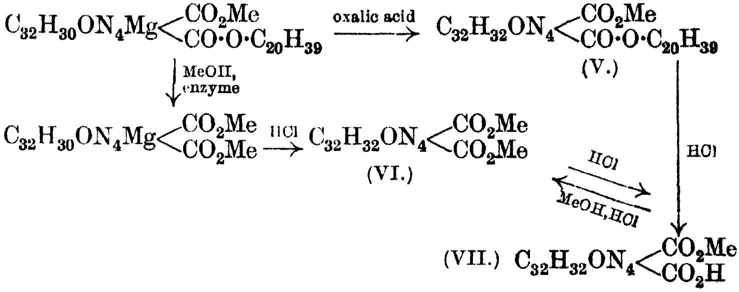
[37] R. Willstätter and M. Utzinger, *Annalen*, 1911, **382**, 129; *A.*, 1911, i, 659.

[38] R. Willstätter, "Chlorophyll," p. 216.

[39] *Ann. Reports*, 1929, **26**, 220.

[40] R. Willstätter, F. Hocheder, and E. Hug, *Annalen*, 1909, **371**, 1; *A.*, 1910, ii, 150.

Phæophorbides.—In 1907, R. Willstätter and F. Hocheder[41] succeeded in removing the magnesium from chlorophyll and the chlorophyllides without secondary decomposition. The olive-brown solids obtained were called phæophorbides. Leaf chlorophyll on treatment with hydrated oxalic acid in alcohol yielded phytyl phæophorbide or phæophytin (V),* and methyl chlorophyllide on treatment with 17% hydrochloric acid in ether was converted into methyl phæophorbide (VI). The action of stronger acid hydrolysed the phytyl group from phæophytin and *one* methyl group from methyl chlorophyllide to yield phæophorbide (VII), which contained a free carboxy-group. Methyl phæophorbide could be obtained by hydrolysis of phæophytin with methyl-alcoholic hydrogen chloride.



$$\begin{tikzcd}
C_{32}H_{30}ON_4Mg{<}\begin{matrix}CO_2Me\\CO\cdot O\cdot C_{20}H_{39}\end{matrix} \arrow[rr, "\text{oxalic acid}"] \arrow[d, "\text{MeOH, enzyme}"] & & C_{32}H_{32}ON_4{<}\begin{matrix}CO_2Me\\CO\cdot O\cdot C_{20}H_{39}\end{matrix}\ \text{(V.)} \arrow[dd, "\text{HCl}"] \\
C_{32}H_{30}ON_4Mg{<}\begin{matrix}CO_2Me\\CO_2Me\end{matrix} \arrow[r, "\text{HCl}"] & C_{32}H_{32}ON_4{<}\begin{matrix}CO_2Me\\CO_2Me\end{matrix}\ \text{(VI.)} \arrow[dr, shift left, "\text{HCl}"] & \\
 & & \text{(VII.)}\ C_{32}H_{32}ON_4{<}\begin{matrix}CO_2Me\\CO_2H\end{matrix} \arrow[ul, shift left, "\text{MeOH, HCl}"]
\end{tikzcd}$$

These substances were obtained as mixtures of *a* and *b* compounds which could be separated by partition between ether and hydrochloric acid. The separation of phæophorbide *a* and *b* is very important in practice, as it is more easily carried out than that of the magnesium-containing compounds.

These reactions reveal a considerable difference in ease of hydrolysis of the two ester groups. Esters of the carboxy-group which carries the phytyl group in chlorophyll are readily hydrolysed, whereas the original carbomethoxy-group present in the natural pigments remains intact.

Although the phytol-free compounds can easily be obtained crystalline, the determination of their molecular formulæ has given some difficulty. The formulæ shown above all contain 5 atoms of oxygen, following Willstätter. When the study of chlorophyll was renewed by H. Fischer and J. B. Conant, both investigators at first preferred formulæ containing 6 atoms of oxygen.[42] In 1932, however, A. Stoll and E. Wiedemann reaffirmed the O_5 formulæ [43] and these were also adopted independently by both the other schools.[44]

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[41] *Annalen*, 1907, **354**, 205; *A.*, 1907, i, 959; "Chlorophyll," Chap. XV.

* The formulæ (V—VII) are for the *a* series.

Acid Separation (Willstätter).[45]—Similar substances of the chlorophyll or of the porphyrin series are separated by means of their difference in basicity, an ethereal solution of the material being extracted successively with hydrochloric acid of increasing strength. This procedure cannot be used with compounds containing labile metals, such as chlorophyll itself, unless the elimination of metal is immaterial. The acid number of a substance is defined as the percentage concentration of hydrochloric acid which extracts two-thirds of it from an equal volume of an ethereal solution: methyl phæophorbide *a* has an acid number of 16 and is completely extracted by 18% acid, whereas methyl phæophorbide *b*, with an acid number of 21, requires 23% acid for complete removal. Extraction of an ethereal solution of methyl phæophorbide $a + b$ with 17% acid therefore leads to almost complete separation. Solutions of the sodium phosphates also are used for such separations.

Chlorin e.—Willstätter found that, when either phæophytin or phæophorbide is hydrolysed by boiling methyl-alcoholic caustic potash for 30 seconds, phytochlorin *e* (*a* series) and phytorhodin *g* (*b* series) are formed.[46] These can be separated by acid fractionation or the individual substances can be prepared from the separated phæophorbides.

From this point it is convenient to concentrate on the compounds of the *a* series. These have received much fuller study because they are more accessible and crystallise better.

The conversion of phæophorbide *a* into chlorin *e* (VIII) involves the hydrolysis of the stable methyl ester group and the addition of a molecule of water:

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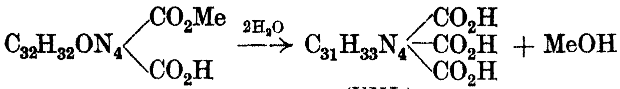
[42] H. Fischer and R. Bäumler, *Annalen*, 1929, **474**, 69; *A.*, 1929, 1185; J. B. Conant and J. F. Hyde, *J. Amer. Chem. Soc.*, 1929, **51**, 3668; *A.*, 1930, 225.

[43] On the occasion of the celebration of Willstätter's 60th birthday; *Naturwiss.*, 1932, **20**, 628. The analytical figures were published later (*Helv. Chim. Acta*, 1933, **16**, 202, 739; *A.*, 1933, 287, 838).

[44] H. Fischer and H. Siebel, *Annalen*, 1932, **499**, 84; *A.*, 1932, 1263; compare H. Fischer, O. Moldenhauer, and O. Süs, *ibid.*, 1931, **486**, 158; *A.*, 1931, 744; J. B. Conant and C. F. Bailey, *J. Amer. Chem. Soc.*, 1933, **55**, 797; J. B. Conant and E. M. Dietz, *ibid.*, p. 839; *A.*, 1933, 1403.

[45] "Chlorophyll," p. 262.

[46] These substances are now generally called chlorin *e* and rhodin *g* respectively. The suffixes date from the time when series of chlorins and rhodins (of doubtful homogeneity) were obtained by acid fractionation. Only chlorin *e* need be considered here.



$$C_{32}H_{32}ON_4\begin{cases}CO_2Me\\CO_2H\end{cases}\xrightarrow{2H_2O}C_{31}H_{33}N_4\begin{cases}CO_2H\\CO_2H\\CO_2H\end{cases}+MeOH$$

(VIII.)

Chlorin *e* is a tribasic acid and yields the same characteristic trimethyl ester by the action of methyl sulphate on the potassium salt[47] and by treatment with diazomethane.[48] This shows that the fifth oxygen atom in phæophorbide is part of a ψ-acidic group. Willstätter interpreted the reaction as the opening of a lactam ring, a suggestion later adopted by J. B. Conant and E. M. Dietz,[49] whereas Fischer regards it as the fission of a cyclic β-ketonic ester. These suggestions will be considered later.

The three carboxy-groups of chlorin *e* are dissimilar, and two monomethyl and two dimethyl esters have been obtained by partial esterification of the free acid and partial hydrolysis of the trimethyl ester.[50] Fischer has recently found that phæophorbide and methyl phæophorbide both yield the trimethyl ester of chlorin *e* on standing with diazomethane in methyl alcohol.[51] This remarkable reaction involves a methanolysis catalysed by the diazomethane; when ethyl alcohol is used as solvent, the ψ-acidic oxygen emerges as a carbethoxy-group.

Chlorin *e* and rhodin *g* are only obtained by the alkaline hydrolysis of phæophorbides under conditions which prevent (or delay) atmospheric oxidation (see p. 385). In the presence of oxygen these and other derivatives of chlorophyll undergo the "phase test." This is a colour reaction which occurs when an ethereal solution of chlorophyll, a phorbide, a phyllide, or chlorin *e* (tri-ester) is shaken with methyl-alcoholic potash. The colour changes to a bright yellow-brown and then back to green (Molisch). Chlorophyll derivatives which show this change are said to be phase-positive.

A reaction analogous to the formation of chlorin *e* is observed with chlorophyll itself. Hot potash under suitable conditions converts this into *iso*chlorophyllins as tripotassium salts. The phytyl and methyl groups are hydrolysed and the ψ-acidic group fixes the third potassium atom. The magnesium is not affected. *iso*-Chlorophyllin *a* (IX) yields chlorin *e* on treatment with acids.

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[47] R. Willstätter and M. Utzinger, *Annalen*, 1911, **382**, 171; *A.*, 1911, i, 659; compare H. Fischer and O. Moldenhauer, *ibid.*, 1930, **478**, 54; *A.*, 1930, 482.

[48] A. Treibs and E. Wiedemann, *ibid.*, 1928, **466**, 264; 1929, **471**, 146; *A.*, 1928, 1383; 1929, 941.

[49] *J. Amer. Chem. Soc.*, 1933, **55**, 839; *A.*, 1933, 403.

[50] H. Fischer and H. Siebel, *Annalen*, 1932, **499**, 84; *A.*, 1932, 1263; J. B. Conant and K. F. Armstrong, *J. Amer. Chem. Soc.*, 1933, **55**, 829; *A.*, 1933, 403.

[51] H. Fischer, W. Gottschaldt, and G. Klebs, *Annalen*, 1932, **498**, 194; *A.*, 1932, 1263; H. Fischer and J. Riedmair, *ibid.*, 1933, **506**, 107; *A.*, 1933, 1308.

$$(\text{I}) \longrightarrow [C_{32}H_{30}ON_4Mg(CO_2H)_2] \longrightarrow \underset{(\text{IX.})^{52}}{C_{31}H_{31}N_4Mg(CO_2K)_3} \xrightarrow{\text{acid}} (\text{VIII})$$

Vigorous Degradation by Alkali.—The conversion of chlorophyll derivatives into porphyrins by the action of alkali at high temperatures was first achieved by E. Hoppe-Seyler,[53] E. Schunck,[54] and E. Schunck and L. Marchlewski.[55] Willstätter and his collaborators [56] found that the action of methyl-alcoholic potash and pyridine on *iso*chlorophyllins under pressure at 140—190° led to graded decarboxylation and the formation of a series of magnesium-containing phyllins. These could be separated through their potassium or ammonium salts. Acid eliminated the magnesium from the phyllins with the formation of the corresponding porphyrins (H_2 for Mg). The third carboxy-group could not be eliminated in this way and the final product was phyllophyllin, $C_{31}H_{33}N_4Mg{\cdot}CO_2H$, the porphyrin corresponding to which (phylloporphyrin) had already been isolated by the earlier workers.[53, 54, 55]

The alkaline degradation of the corresponding magnesium-free compounds, particularly of chlorin *e*, yielded a series of porphyrins which could be separated by the Willstätter method.[57, 58, 59] There is some difference between the results of the various schools regarding the intermediate substances isolated in this reaction, but general agreement on the main final products. These are three porphyrins of known constitution : two are monocarboxylic acids, phylloporphyrin, $C_{31}H_{35}N_4{\cdot}CO_2H$ (already mentioned), and pyrroporphyrin, $C_{30}H_{33}N_4{\cdot}CO_2H$, and one a dicarboxylic acid, rhodoporphyrin, $C_{30}H_{32}N_4(CO_2H)_2$. It was first thought that the two monocarboxylic acids were isomeric, but it is now known that phylloporphyrin is a methyl pyrroporphyrin. Rhodoporphyrin is a carboxypyrroporphyrin and can readily be decarboxylated to

[52] Probable constitution; cf. " Chlorophyll," Chap. XVIII.

[53] *Z. physiol. Chem.*, 1879, **3**, 339; 1880, **4**, 193; *A.*, 1880, 53, 894.

[54] *Proc. Roy. Soc.*, 1891, **50**, 302.

[55] *Ibid.*, 1895, **57**, 314; *Annalen*, 1894, **284**, 81; *A.*, 1894, i, 341; 1895, i, 296.

[56] R. Willstätter and A. Pfannenstiel, *ibid.*, 1907, **358**, 205; R. Willstätter and H. Fritzsche, *ibid.*, 1909, **371**, 33; *A.*, 1908, i, 198; 1910, i, 126. Willstätter also studied the corresponding degradations of allomerised chlorophyll.

[57] R. Willstätter, " Chlorophyll," p. 353.

[58] H. Fischer and A. Treibs, *Annalen*, 1928, **466**, 188; *A.*, 1928, 1382.

[59] A. Treibs and E. Wiedemann, *ibid.*, p. 264; *A.*, 1928, 1383.

pyrroporphyrin. Phylloporphyrin can be converted into pyrroporphyrin by drastic treatment with alkali.

The last carboxy-group in pyrro- and phyllo-porphyrins (and in the corresponding phyllins) is very stable. Decarboxylation is best effected by dry distillation with soda-lime [56, 60] or by pyrolysis of the free acids alone or in high-boiling solvents.[58] In this way the oxygen-free parent substances of the group are obtained; phylloporphyrin yields phylloætioporphyrin, $C_{31}H_{36}N_4$, and pyrroporphyrin yields pyrroætioporphyrin, $C_{30}H_{34}N_4$. Phylloætioporphyrin is degraded to pyrroætioporphyrin by sodium ethoxide at a high temperature.[58] The corresponding magnesium compound, (pyrro)ætiophyllin, has been obtained by decarboxylating rhodophyllin.[61]

$$\begin{tikzcd}
 & \text{Phylloporphyrin} \arrow[r, "-CO_2"] \arrow[dd, "\text{alkali}"', "(-CH_2)"] & \text{Phylloætioporphyrin} \arrow[dd, "\text{NaOEt}"', "(-CH_2)"] \\
\text{Chlorin } e \arrow[ur, "(-C_2O_4)"] \arrow[d, "(-C_2H_2O_2"] & & \\
\text{Rhodoporphyrin} \arrow[r, "(-CO_2)"] & \text{Pyrroporphyrin} \arrow[r, "-CO_2"] & \text{Pyrroætioporphyrin}
\end{tikzcd}$$

It was at first thought [61] that the ætioporphyrins from chlorophyll were identical with that derived from the blood pigment (mesoætioporphyrin). This has been shown to be incorrect by Hans Fischer. Nevertheless these chlorophyll porphyrins resemble the porphyrins of the hæmin series in general properties and are red, crystalline solids with low acid numbers. They are simply inter-related, but the reaction by which they are formed from chlorin *e* is comparatively complex, as will be seen later. We have now left the exact chlorophyll type, but are approaching substances of known constitution.

Degradation to Pyrroles.—The drastic oxidation of intact chlorophyll has given no useful results, probably on account of complications arising from the presence of the phytyl group. Following W. Küster's classical work on the oxidation of hæmin,[62] L. Marchlewski oxidised phylloporphyrin with chromic acid to the nitrogen-free anhydride, $C_8H_8O_5$, corresponding to hæmatic acid (X, O for NH).[63] R. Willstätter and Y. Asahina [64] found that rhodo-, phyllo-, and pyrro-porphyrins and chlorin *e* gave the same mixture of methylethylmaleinimide (XI) and hæmatic acid (X)

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[60] R. Willstätter and Max Fischer, *Z. physiol. Chem.*, 1913, **87**, 430; *A.*, 1913, i, 1251.

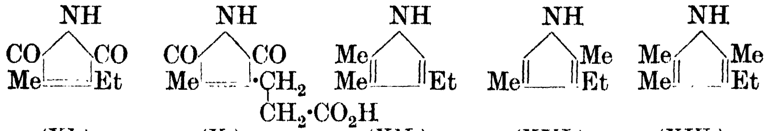
[61] *Idem*, *Annalen*, 1913, **400**, 182; *A.*, 1913, i, 1218.

[62] *Z. physiol. Chem.*, 1899, **28**, 1, etc.; *A.*, 1900, i, 68.

[63] *J. pr. Chem.*, 1902, [ii], **65**, 161; *A.*, 1902, i, 387.

[64] *Annalen*, 1910, **373**, 227; *A.*, 1910, i, 499.

when oxidised by chromic acid, Caro's acid, or lead peroxide. The structures of these were already known.



(XI.) (X.) (XII.) (XIII.) (XIV.)

One molecule of the chlorophyll derivative yielded rather less than one molecule of the acid (X) but considerably more than one molecule of the imide (XI).

Following preliminary work by M. Nencki and L. Marchlewski,[65] R. Willstätter and Y. Asahina reduced phylloporphyrin with hydrogen iodide and acetic acid under drastic conditions to hæmopyrrole (XII), kryptopyrrole (XIII), and phyllopyrrole (XIV).[66] Ethyl chlorophyllide was reduced similarly to a mixture of dimethylethylpyrroles, and chlorin *e* to crude hæmopyrrole and phyllopyrrole. The yields in all these degradations were noticeably worse than those encountered in the hæmin series. It was subsequently observed by H. Fischer, A. Merka, and E. Plötz [67] that chlorophyll, unlike hæmin, gave on reduction with hydriodic acid about one molecular proportion of carbon dioxide, corresponding to the presence of a labile carboxyl group.

The general conclusions from these results are that at least three pyrrole rings are present in the molecule of chlorophyll and its derivatives, that one pyrrole carries a methyl group and a propionic acid group in the β-position, that two pyrroles carry methyl and ethyl groups in the β-position, and that the pyrrole rings are joined through carbon atoms (such as methene groups) in the α-position.

Structure of Rhodo-, Phyllo-, and Pyrro-porphyrins.—We now turn to Fischer's brilliant synthetic work in the field. The existence of four stable nitrogen atoms in the molecule and the drastic degradation to pyrroles suggested that phylloporphyrin and its associates belonged to the porphyrin series. Moreover, the absorption spectrum of pyrroporphyrin, and to a less extent of phylloporphyrin, was close to that of the porphyrins of the blood series, such as mesoporphyrin. If the parent ætioporphyrin of the chlorophyll series were identical or isomeric with that of the hæmin series, it seemed possible that pyrroporphyrin (and phylloporphyrin, which was then thought to be isomeric with it) might be a simple monocarboxylated derivative, namely, a tetramethyltriethylporphinpropionic acid [68] such as (XV). (It is true that this would mean that pyrroporphyrin would contain 33 instead of 31 carbon atoms, but analysis could not decide definitely on this point.) The eight possible isomeric acids of this type were synthesised by Fischer and his co-workers [69,70] and characterised by the melting points of their methyl esters and in other ways. None was identical with either pyrro- or phyllo-porphyrin.

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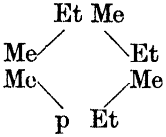
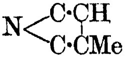
[65] *Ber.*, 1901, **34**, 1687; *A.*, 1901, i, 554.

[66] *Annalen*, 1911, **385**, 188; *A.*, 1912, i, 41.

[67] *Ibid.*, 1930, **478**, 283; *A.*, 1930, 620.

(XV.) 

(p = $CH_2{\cdot}CH_2{\cdot}CO_2H$ here and subsequently.)

At about the same time it was found by A. Treibs and E. Wiedemann [59] that pyrroporphyrin could be brominated to a monobromo-compound which yielded bromocitraconimide on oxidation. Hence pyrroporphyrin contained at least one ring of the type  $N\begin{matrix}\diagup C{\cdot}CH \\ \diagdown C{\cdot}CMe\end{matrix}$ and was probably a tetramethyldiethylporphinpropionic acid. It was possible to test this by subjecting the free methene group to a series of reactions resembling that used in the synthesis of hæmin,[71] namely, $R{\cdot}H \longrightarrow R{\cdot}COMe \longrightarrow R{\cdot}CH(OH)Me \longrightarrow R{\cdot}CH{:}CH_2 \longrightarrow R{\cdot}Et$ (where R = tetramethyldiethylporphinpropionic acid, less H). By this process pyrroporphyrin was converted into one of the tetramethyltriethylporphinpropionic acids already synthesised. The acid actually obtained [70] (methyl

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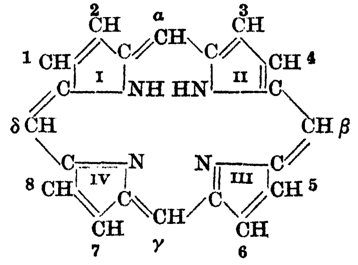
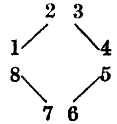
[68] The methene groups and pyrrole rings of porphin are numbered and lettered as shown in (XVI). The placing of the hydrogens on the nitrogen atoms, and the consequent position of the double bonds, is arbitrary. For the purpose of indicating the position of substituents, the formula is most conveniently abbreviated to (XVI*a*), where the lines represent the $\beta\beta$-sides of the four pyrrole rings.

(XVI.) 



(XVI*a*.)

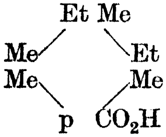
[69] H. Fischer, H. Grosselfinger, and G. Stangler, *Annalen*, 1928, **461**, 221; *A.*, 1928, 651.

[70] H. Fischer, H. K. Weichmann, and K. Zeile, *ibid.*, 1929, **475**, 241; *A.*, 1929, 1465.

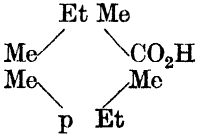
[71] See *Ann. Reports*, 1932, **29**, 209.

ester, m. p. 271°) was identical with the synthetic acid of formula (XV), in which the orientation of the groups followed from the method of synthesis. This at once proved that pyrroporphyrin was a tetramethyldiethylporphinpropionic acid. It was uncertain which of the ethyl groups of the triethyl compound had been introduced by the acetylation and subsequent treatment and which were the two already present in the pyrroporphyrin. The free methene group of the latter could, however, only be at C_2, C_4, or C_6.

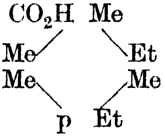
This was settled by an examination of rhodoporphyrin. As has been stated, this substance contains two carboxy-groups, one of which is easily removed with the formation of pyrroporphyrin. It was known from work in the hæmin series that ω-carboxylic acids of the porphyrin series (*e.g.*, the large class which contains the carboxy-group at the end of a nuclear ethyl group, as $—CH_2{\cdot}CH_2{\cdot}CO_2H$) are only decarboxylated with great difficulty. As the labile carboxy-group of rhodoporphyrin was not substituted in an alkyl group, it was presumably nuclear, being placed on the free methene group of pyrroporphyrin. Rhodoporphyrin was therefore either (XVII), (XVIII), or (XIX).



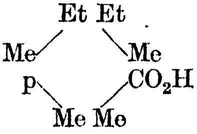
(XVII.)



(XVIII.)



(XIX.)



(XX.)

It was known from the study of natural and synthetic uroporphyrins that the absorption spectra of compounds with adjacent carboxy-groups differed slightly from those in which the carboxy-groups were separated by alkyls. Comparison of the spectrum of " natural " rhodoporphyrin with that of a synthetic isomeride (XX) showed the same difference and indicated that in rhodoporphyrin the nuclear carboxyl was on C_6, next to the propionic acid group.[72]

This was confirmed by synthesis. Synthetic 1 : 3 : 5 : 8-tetramethyl-2 : 4-diethyl-6-carboxyporphin-7-propionic acid (XXI; $A = CO_2H$, $B = CH_2{\cdot}CH_2{\cdot}CO_2H$) was identical with rhodoporphyrin. The corresponding compound without the 6-carboxy-group (XXI; $A = H$, $B = CH_2{\cdot}CH_2{\cdot}CO_2H$) was also synthesised, and proved to be identical with pyrroporphyrin.[73] It followed that the completely decarboxylated pyrroætioporphyrin was 1 : 3 : 5 : 8-

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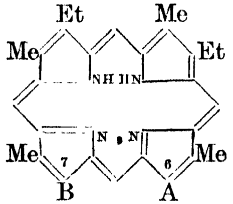
[72] H. Fischer and A. Schormüller, *Annalen*, 1929, **473**, 211; *A.*, 1929, 1184.

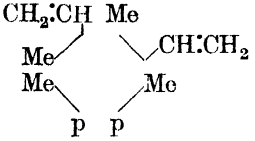
[73] H. Fischer, H. Berg, and A. Schormüller, *ibid.*, 1930, **480**, 109, 189; **482**, 232; *A.*, 1930, 931; 1931, 101.

tetramethyl-2 : 4 : 7-triethylporphin (XXI; A = H, B = Et). This also was proved by synthesis.[73]

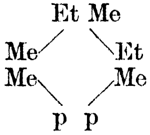


(XXI.)

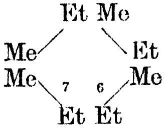
The very important fact emerges that the parent porphyrins of the hæmin and chlorophyll series are closely related in structure.[74] Hæmin is the ferric (chloride) derivative of protoporphyrin (XXII).[71] On reduction the latter gives mesoporphyrin (XXIII), which on decarboxylation yields ætioporphyrin-III (XXIV). This has exactly the same substituents, except on C_6, as pyrroætioporphyrin and is in fact 6-ethylpyrroætioporphyrin. This relationship is of considerable biological significance.



(XXII.)



(XXIII.)



(XXIV.)

The similarity between the two series suggested the possibility of interconversion and this was realised by Fischer in both directions. Pyrroporphyrin was converted into mesoporphyrin, identical with that obtained from hæmin,[75] by a complicated series of reactions, in which the essential changes on C_6 were the following:

$$\mathrm{R{\cdot}H} \xrightarrow{\mathrm{CH_2Cl{\cdot}OMe,SnCl_4}} \mathrm{R{\cdot}CH_2{\cdot}OMe} \xrightarrow{\mathrm{HBr}} \mathrm{R{\cdot}CH_2Br} \xrightarrow{\text{potassiomalonate}}$$

$$\mathrm{R{\cdot}CH_2{\cdot}CH(CO_2Me)_2} \xrightarrow[\text{decarboxylation}]{\text{hydrolysis,}} \mathrm{R{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$$

Mesoporphyrin dimethyl ester has been degraded to a pyrroporphyrin,[76] isomeric with the "natural" compound, with the C_6 and C_7 groups reversed.

Phylloporphyrin, which is richer by CH_2 than pyrroporphyrin, must contain a similar disposition of nuclear substituents, as it yields the latter with sodium ethoxide. The most probable structure was that having two of the pyrrole rings joined, not by an α-methene group as in the simple porphyrins, but by the group —CMe=.[77] There are four dissimilar methene bridges (α, β, γ, δ in formula XVI) in pyrroporphyrin, so four bridge-methyl derivatives are possible. These were all synthesised; the substance with the methyl group on C_γ (XXV) was identical with phylloporphyrin from natural sources.[78] It followed that phylloætioporphyrin had the analogous structure with an ethyl group for $—CH_2·CH_2·CO_2H$ on C_7.

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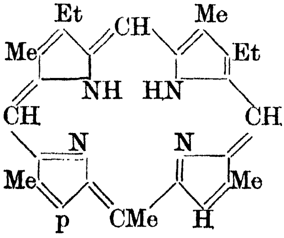
[74] Verdeil's claim (*Compt. rend.*, 1851, **33**, 689) that the pigments of the leaf and the blood were related was thus prophetic, although based on invalid experimental work.

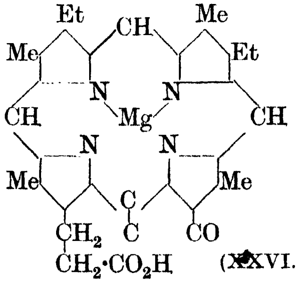
[75] H. Fischer and H. J. Riedl, *Annalen*, 1931, **486**, 178; *A.*, 1931, 744.

[76] H. Fischer and J. Ebersberger, *ibid.*, 1934, **509**, 19; *A.*, 1934, 421.

If the structure of the porphyrins be held to be proved by these syntheses,[79] the question arises as to how far we can apply this knowledge to the structure of chlorophyll itself. Willstätter pointed out the need for caution here, because the vigorous alkaline degradation may cause some deep-seated change in the molecule. Nevertheless several facts suggest that the relationship is fairly close: (i) The same porphyrins and not isomerides are always obtained as final products in the alkaline degradation; the order of substituents remains the same, and hence it is unlikely that there has been a ring fission and resynthesis. (ii) Some of the reagents which convert chlorin *e* into phylloporphyrin are comparatively mild, *e.g.*, boiling quinoline, phosphoric acid at 140°.[80]



(XXV.)



(XXVI.)

On the hypothesis of a fairly close structural resemblance, we arrive at the skeleton (XXVI) for chlorophyll *a*,[81] in which the double bonds are neglected. The magnesium atom is placed on two pyrrole nitrogen atoms by analogy with the iron of hæmin and because the existence of ætiophyllin shows that the metal can be combined independently of oxygen. If to the formula of pyrroporphyrin the methyl and phytyl groups and the magnesium atom are added and the four hydrogens which these groups replace are subtracted, a formula is obtained which differs from that of chlorophyll *a* ($C_{55}H_{72}O_5N_4Mg$) by (C_3O_3) :

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[77] A —CH=CH— bridge was also considered by Fischer, but was abandoned in view of the synthetic results.

[78] H. Fischer and H. Helberger, *Annalen*, 1930, **480**, 235; *A.*, 1930, 932; H. Fischer, W. Siedel, and L. Le Thierry d'Ennequin, *ibid.*, 1933, **500**, 137; *A.*, 1933, 286.

[79] The evidence is strong but not final (see p. 360).

[80] R. Willstätter and M. Utzinger, *Annalen*, 1911, **382**, 171; *A.*, 1911, i, 659.

[81] This should be compared with the formulæ advanced by Fischer, Conant, and Stoll (p. 379).

$$[C_{31}H_{34}O_2N_4 + CH_3 + C_{20}H_{39} + Mg - 4H = C_{52}H_{72}O_2N_4Mg].$$

From the formation of phyllo- and rhodo-porphyrins we may place a carbon atom on C_γ and an oxygen-carrying carbon atom on C_6. If allowance is made for the hydrogen atoms replaced, the unlocated substituents become (CH_2O_2), which may be presumed to be attached to the substituents on C_6 and C_γ. Further, chlorophyll *a* contains two carboxy-groups, carrying the phytyl and a methyl group. One of these is located in the propionic acid group on C_7; the other must presumably form part of the "6γ-system." Actually the structural position is more complicated than is indicated by this summary, because the fundamental ring system of chlorophyll, the phorbides, and chlorins differs slightly from that of the derived porphyrins.

The next stage in the elucidation of the structure was the establishing by less drastic reagents of the connection between chlorophyll and the porphyrins. A suitable reagent was found by Fischer [82] in a mixture of hydriodic and acetic acids. At about 60° this reduced phæophorbide *a* to a leuco-compound, aerial oxidation of which gave a series of phæoporphyrins, which contained the same number of carbon atoms as the initial material (34, neglecting the ester group). The exact products formed varied with the conditions of reaction. Similar treatment of chlorin *e* or its trimethyl ester gave another series of C_{33} and C_{34} porphyrins, the chloroporphyrins. The most important compounds of these two series are shown below; the formulæ are stripped of ester groups to facilitate comparison.[83]

From phæophorbide *a*, ($C_{34}H_{34}O_5N_4$) :

Oxyphæoporphyrin a_5,[84] $C_{34}H_{34}O_6N_4$ } Isolated as monomethyl
Phæoporphyrin a_5, $C_{34}H_{34}O_5N_4$ } esters.

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[82] H. Fischer and R. Bäumler, *Annalen*, 1929, **474**, 65; 1930, **480**, 197; *A.*, 1929, 1185; 1930, 932; H. Fischer and O. Moldenhauer, *ibid.*, 1930, **478**, 54; H. Fischer, A. Merka, and E. Plötz, *ibid.*, p. 284; *A.*, 1930, 482, 620; K. Noack and W. Kiessling, *Z. physiol. Chem.*, 1929, **182**, 36; *A.*, 1929, 727.

[83] A useful summary of their formation and properties is given by Fischer in Oppenheimer's "Handbuch der Biochemie," Ergänzungswerk I, 1933, 266—267.

[84] Originally called neophæoporphyrin a_6. The corresponding ethoxyphæoporphyrin a_5 was originally called phæoporphyrin a_6.

From chlorin e, ($C_{34}H_{36}O_6N_4$) :

Chloroporphyrin e_6, $C_{34}H_{36}O_6N_4$	Isolated as monomethyl ester.
Chloroporphyrin e_5, $C_{33}H_{34}O_5N_4$ Chloroporphyrin e_4, $C_{33}H_{36}O_4N_4$	Isolated as free acids.

[The suffixes a and e denote the derivation from phæophorbide a and chlorin e respectively. The numbers which follow denote the number of atoms of oxygen in the molecule.]

These compounds crystallise well and yield polymethyl esters when treated with diazomethane. The two series differ in absorption spectra. It should be noted that the stable methyl ester group of chlorophyll a persists in three of the compounds named in the list.

The most important from the structural point of view is phæoporphyrin a_5, which is isomeric with phæophorbide a and, like it, is a monomethyl ester, but differs from it in absorption spectrum and other properties.[85] It yields a monoxime. It was also formed from phæophorbides by catalytic hydrogenation over platinum, followed by aerial oxidation of the leuco-compounds formed.[86] J. B. Conant and J. F. Hyde also showed that the near derivatives of chlorophyll could be converted into porphyrins in this way.[87]

Phæoporphyrin a_5 readily loses its carbomethoxy-group and yields phylloerythrin, $C_{33}H_{34}O_3N_4$, a substance of great importance, first discovered by L. Marchlewski.[88] This may be obtained direct from chlorophyllide and the phæophorbides by the prolonged action of boiling 20% hydrochloric acid and also by the biological degradation of chlorophyll. It has been found in ox-bile, the fæces of ruminants, elephants and other herbivora, and in cattle gall-stones.[89] The best source is sheep dung. It is extremely stable and its chemical properties and absorption spectrum show it to be a porphyrin. The formation of a porphyrin by a simple biological process shows independently that chlorophyll contains a basic structure very like that of the porphyrins.[90]

The actual process in the digestive tract is one of isomerisation and decarboxylation, and appears to be confined to the higher animals. A number of other degradation products of chlorophyll *in vivo* have been discovered, *e.g.*, probophorbides (sheep dung) and phyllobombycin (fæces of silk-worms). These contain a modified porphyrin system.

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[85] H. Fischer and O. Süs, *Annalen*, 1930, **482**, 225; *A.*, 1931, 102.

[86] H. Fischer and H. Helberger, *ibid.*, 1930, **480**, 260; *A.*, 1930, 932; H. Fisher and E. Lakatos, *ibid.*, 1933, **506**, 123; *A.*, 1933, 1308; compare E. M. Dietz and T. H. Werner, *J. Amer. Chem. Soc.*, 1934, **56**, 2180; *A.*, 1934, 1371.

[87] *Ibid.*, 1930, **52**, 1233; *A.*, 1930, 799.

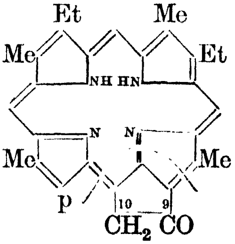
[88] *Z. physiol. Chem.*, 1929, **185**, 8; *A.*, 1929, 1468.

[89] H. Fischer and R. Hess, *ibid.*, 1930, **187**, 133; *A.*, 1930, 634.

[90] Early evidence of the close connection between the green derivatives of chlorophyll and the porphyrins comes also from J. B. Conant and J. F. Hyde's demonstration that porphyrins were produced by the pyrolysis of chlorin e (*J. Amer. Chem. Soc.*, 1929, **51**, 3668; *A.*, 1930, 225).

The structure of phylloerythrin has been established by Fischer both analytically [91,92] and by synthesis. One of the oxygen atoms is ketonic; the oxime on reduction by the Kishner–Wolff method gives deoxophylloerythrin ($C_{33}H_{36}O_2N_4$), in which the two remaining oxygens are present as carboxyl. Deoxophylloerythrin can be obtained directly from phæophorbide *a* by treatment with hydrogen bromide in acetic acid at 180°. It is not identical with any of the isomeric tetramethyltriethylporphinpropionic acids, which only differ from it in formula by two hydrogen atoms. Phylloerythrin on treatment with sodium ethoxide in presence of air yields phyllo-, pyrro-, and rhodo-porphyrins.

Fischer's interpretation of these facts, which is generally accepted, is that in both phylloerythrin (XXVII) and its deoxo-compound (XXVII, CH_2 for CO), the C_6 and C_γ carbon atoms form part of a five-membered carbon ring.



(XXVII.)

The presence of this was shown by the synthesis of deoxophylloerythrin.[93] The relationship between the two substances was confirmed by the oxidation of deoxophylloerythrin to phylloerythrin by oleum containing sulphur.[94] The yield was poor and some chloroporphyrin e_5 was formed by further oxidation. The position of the carbonyl group at C_9 in phylloerythrin follows from its fission by alkali into phylloporphyrin and rhodoporphyrin, which recalls that of deoxybenzoin into benzoic acid and toluene : $R\cdot CH_2\cdot COR' \longrightarrow R\cdot CH_3 + HO\cdot OC\cdot R'$.

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[91] H. Fischer, O. Moldenhauer, and O. Süs, *Annalen*, 1931, **485**, 1; *A.*, 1931, 496.

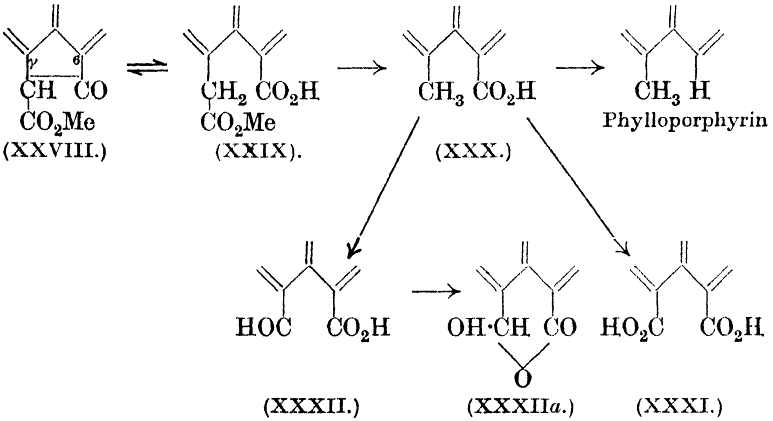
[92] *Idem*, *ibid.*, 1931, **486**, 107; *A.*, 1931, 744.

[93] H. Fischer and J. Riedmair, *ibid.*, 1931, **490**, 91; 1932, **497**, 181; *A.*, 1931, 1431; 1932, 1045.

[94] H. Fischer, J. Heckmaier, and J. Riedmair, *ibid.*, 1932, **494**, 86; *A.*, 1932, 625.

The structure of deoxophylloerythrin has been confirmed by its synthesis from phylloporphyrin.[95] The latter was converted into its hæmin (ferric compound), and a $CH_2 \cdot OMe$ group introduced on C_6 by means of chloromethyl ether and stannic chloride. The product was freed from iron and purified by successive treatment with hydrogen bromide and alkali. The oxymethyl porphyrin was finally converted into deoxophylloerythrin by fusion with succinic acid, which eliminated methyl alcohol and formed the 9 : 10-bond.

Phæoporphyrin a_5 (XXVIII) was recognised by Fischer as the β-ketonic ester corresponding to phylloerythrin,[92] a view accepted by Conant and Stoll. When hydrolysed with acid or cold alcoholic potash, it underwent ring fission of the usual *cyclo*pentanonecarboxylate type and yielded chloroporphyrin e_6, the methyl hydrogen ester of the corresponding open-chain (adipic) acid (XXIX) :



[These partial formulæ show the portion of the molecule below the dotted line in (XXVII), the rest of the molecule being the same.]

The methyl hydrogen ester (XXIX) can be cyclised back to (XXVIII) by rather unusual reagents: pyridine and sodium carbonate, or a mixture of hydriodic and acetic acids. Formic acid removes the carbomethoxy-group from chloroporphyrin e_6 to give chloroporphyrin e_4 (XXX), which can be further decarboxylated to phylloporphyrin. Chloroporphyrin e_4 is therefore γ-methylrhodoporphyrin (or phylloporphyrin-6-carboxylic acid) and chloroporphyrin e_6 is the ester of rhodoporphyrin-γ-acetic acid. The presence of the 6-carboxyl makes the methyl group of γ-methylrhodoporphyrin very easily oxidisable (contrast phylloporphyrin); according to the conditions it yields chloroporphyrin e_5 (γ-formylrhodoporphyrin, XXXII; which appears to exist normally in the cyclic form XXXII*a*) or rhodoporphyrin-γ-carboxylic acid (XXXI). The latter is also formed by the action of oxygen and alkali on phylloerythrin. A number of other transformations of these porphyrins have been studied by Fischer.[85, 91, 92, 94]

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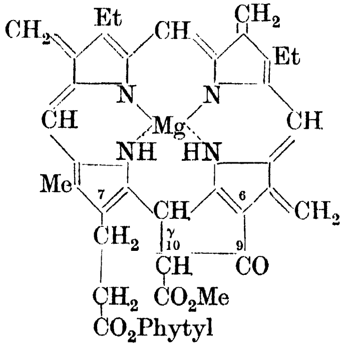
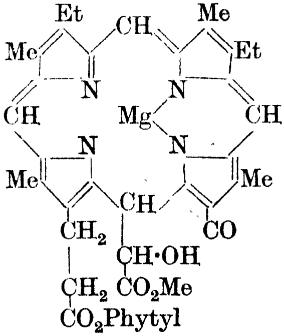
[95] H. Fischer, M. Speitmann, and H. Meth, *Annalen*, 1934, **508**, 154; *A.*, 1934, 308.

Fischer's view that phæophorbide *a* and phæoporphyrin a_5 (monoester) on the one hand, and chlorin *e* and chloroporphyrin e_6 on the other, are pairs of isomerides has not been accepted by J. B. Conant, who regards the chlorophyll derivatives as being richer in hydrogen than the porphyrins. This point cannot be settled by analysis, but calorimetric determinations by A. Stern and G. Klebs [96] support the idea of isomerism. In any case, it is



(XXXIII.)

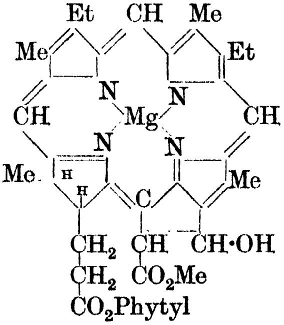
H. Fischer.[97]



(XXXIV.)

J. B. Conant.[98]

(XXXV.)



A. Stoll.[99]

[96] *Annalen*, 1933, **505**, 295; *A.*, 1933, 1173.

[97] *Ibid.*, 1933, **502**, 175; *A.*, 1933, 617. Revised from several earlier formulæ.

[98] J. B. Conant and E. M. Dietz, *J. Amer. Chem. Soc.*, 1933, **55**, 839; *A.*, 1933, 403. Revised from a previous formula (*ibid.*, 1931, **53**, 2382; *A.*, 1931, 1075). The γ-side chain was believed to be of the type $>C{:}CH{\cdot}CO_2Me \leftrightarrows >CH{\cdot}CH(OH){\cdot}CO_2Me$.

[99] A. Stoll and E. Wiedemann, *Naturwiss.*, 1932, **20**, 706. Experimental results appeared later (*Helv. Chim. Acta*, 1933, **16**, 183; *A.*, 1933, 287, *etc.*).

now clear that chlorophyll and its near derivatives contain a ring system similar to but not identical with that of the porphyrins. This is referred to as the *iso*porphyrin (*iso*porphin) system.

In 1932—1933, the three formulæ for chlorophyll on p. 379 were proposed and it is convenient to consider further investigations in relation to them.

These formulæ have certain common features, based mainly on Fischer's synthetic work, namely, a modified porphin ring, virtually the same arrangement of alkyl substituents in the β-positions of the pyrrole rings, and carbon substituents on C_6 and C_γ. The phytyl group is placed on the propionic acid side chain at C_7, and the methyl group on the C_{10} carboxyl, as first proved by Conant.[1] Fischer proposed the reverse arrangement,[92] but later corrected it.[2] The evidence on this point is briefly as follows : (i) Phæophorbide *a* contains the original carbomethoxy-group of chlorophyll intact and has one free carboxy-group which originally carried the phytyl. On pyrolysis it yields pyrophæophorbide *a* (the phorbide corresponding to phylloerythrin) with loss of the carbomethoxy-group, but the free carboxyl remains intact. Only a β-propionic acid group could survive pyrolysis in this manner. (ii) Ethyl chlorophyllide also contains the original carbomethoxy-group and has ethyl in place of phytyl. Hydriodic acid converts it into the ethyl ester of phæoporphyrin a_5, which on pyrolysis yields phylloerythrin ethyl ester. Hence the ethyl group in ethyl chlorophyllide and the phytyl group in chlorophyll are carried by the propionic acid side chain.

Stoll accepted Fischer's carbocyclic ring, but Conant[98] did not consider that the presence of this in chlorophyll *a* or the phæophorbides was proved by their transformation into phæoporphyrin a_5 and phylloerythrin. He suggested that the ring might be formed during the reaction just as it is in the formation of phylloerythrin from the chloroporphyrins.

All three formulæ differ as to the state of reduction of the molecule and the mode of combination of the fifth oxygen atom. Fischer placed this in a carbonyl group at C_9, Stoll in a secondary alcohol group, and Conant in a lactam ring. Early attempts to prepare ketonic derivatives from chlorophyll *a* and the phorbides of the *a* series had failed, though H. Fischer and J. Riedmair had obtained indirect evidence for the keto-group in the formation of tri-acid derivatives with diazomethane in an atmosphere of nitrogen[3]

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[1] J. B. Conant and J. F. Hyde, *J. Amer. Chem. Soc.*, 1929, **51**, 3668; *A.*, 1930, 225; J. B. Conant, E. M. Dietz, C. F. Bailey, and S. E. Kamerling, *ibid.*, 1931, **53**, 2382; *A.*, 1931, 1075.

[2] H. Fischer, O. Süs, and G. Klebs, *Annalen*, 1931, **490**, 38; *A.*, 1931, 1431.

[3] *Ibid.*, 1933, **506**, 107; *A.*, 1933, 1308.

(which would prevent the oxidation of a secondary alcohol of the type suggested by Stoll). Apparent support for the alcohol formula came from A. Stoll and E. Wiedemann's preparation of a benzoyl derivative from phæophorbide *a* and methyl phæophorbide *a*.[4] The presence of a keto-group was proved independently and conclusively by Fischer [5] and Stoll,[6] who prepared a phase-positive oxime from methyl phæophorbide *a*. This could be converted into the oxime of phæophorbide, phæophorbide itself, or the oxime of phæoporphyrin a_5 according to the conditions. This result led Stoll to abandon the alcohol grouping on C_9 in favour of carbonyl, but he retained the dihydroporphin arrangement of the nucleus. The benzoylation was interpreted as a reaction of the enolic form of the phorbides. The presence of a keto-group in phæophorbide *a* is incompatible with Conant's lactam formula, which is also open to objection on stereochemical grounds.

Fischer's 1933 formula (XXXIII) contained two free imino-groups and three of the methyl groups converted into methylenes (arbitrarily the ones on C_1, C_3, and C_5). Experimental support for the free imino-groups seemed to be provided by Zerewitinoff determinations of active hydrogen, but the method is of doubtful value in this series [7] and in view of subsequent developments the results probably are not significant. Strong evidence has recently been found by Fischer for the presence of unsaturated side chains in chlorophyll and the *iso*porphin derivatives generally, by the "oxo-reaction" and the addition of diazoacetic ester.

H. Fischer and J. Riedmair [8] found that when phæophorbide or methyl phæophorbide was treated with cold hydriodic and acetic acids, best in a steam of oxygen, a crystalline porphyrin, oxophæoporphyrin a_5, containing 6 atoms of oxygen, was formed. In nitrogen the reaction gave the usual phæoporphyrin a_5. The oxo-porphyrin yielded a dioxime and hence contained a second carbonyl group : the reaction was therefore an oxidation in addition to the usual *iso*porphin ⟶ porphin change. The oxo-reaction was also given by chlorin *e*, chlorin e_4 (formed by decarboxylation of chlorin *e* in pyridine), and pyrophæophorbide, but *not* by the derived porphyrins. It was first thought that these oxo-compounds contained an aldehydo-group in place of an unsaturated side chain,[5] but a comparison with synthetic formylporphyrins showed this to be incorrect. Fischer accordingly abandoned the hypothesis that chlorophyll *a* and its near derivatives contained methylene groups (XXXIII) and considered that the oxoporphyrins were monoacetyl compounds in which the acetyl group was derived from a single ethylidene group on C_2 or C_4.[9] The position of this substituent was found as follows : Under the conditions of the oxo-reaction, pyrophæophorbide *a* yielded oxophylloerythrin. When this was heated with hydrochloric acid in a sealed tube, the carbonyl-containing side chain was eliminated and two new porphyrins were formed. These resembled pyrroporphyrin and phylloerythrin respectively but were not identical with them. The first contained two free pyrrole methene groups and was considered to be a de-ethylpyrroporphyrin (such as XXXVI); the second, with one free methene group, was a de-ethylphylloerythrin (such as XXXVII) which could be reduced to the corresponding deoxo-compound, with CH_2 for CO.

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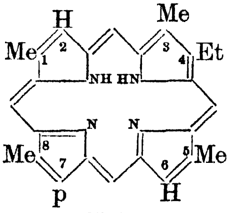
[4] *Helv. Chim. Acta*, 1933, **16**, 739; *A.*, 1933, 838.

[5] H. Fischer, J. Riedmair, and J. Hasenkamp, *Annalen*, 1934, **508**, 224; *A.*, 1934, 420.

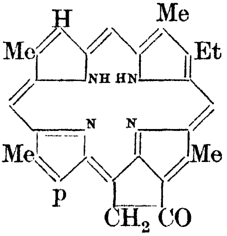
[6] A. Stoll and E. Wiedemann, *Helv. Chim. Acta*, 1934, **17**, 163; *A.*, 1934, 308. There was a polemic as to priority : both the papers cited [5, 6] are dated December, 1933.

[7] H. Fischer and P. Rothemund, *Ber.*, 1931, **64**, [*B*], 201; *A.*, 1931, 497.

[8] *Annalen*, 1933, **505**, 87; *A.*, 1933, 959.



(XXXVI.)



(XXXVII.)

The structure of these was proved by their synthesis by Fischer's general methods. 1 : 3 : 5 : 8-Tetramethyl-4-ethylporphin-7-propionic acid (XXXVI) gave an ester identical with that of the de-ethylpyrroporphyrin from oxophylloerythrin.[10] Both the possible de-ethyldeoxophylloerythrins were synthesised by H. Fischer and W. Rose;[11] the 2-de-ethyl compound (XXXVII; CH_2 for CO) was identical with that prepared from natural sources.[12] It follows that the oxo-group in the oxoporphyrins, and hence the unsaturated side chain in the phorbides, is in the 2-position. The nature of the oxo-group was proved as follows. The ester of 2-de-ethylpyrroporphyrin (XXXVI) was converted into the hæmin (ferric) compound and acetylated to a diacetyl derivative ($CH_3{\cdot}CO$ for H at C_2 and C_6). The same compound was formed by the acetylation

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[9] H. Fischer and J. Hasenkamp, *Annalen*, 1934, **513**, 107; *A.*, 1934, 1370.

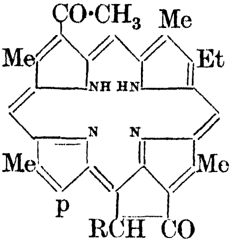
[10] H. Fischer and S. Böckh, *ibid.*, 1935, **516**, 177; *A.*, 633.

[11] *Ibid.*, 1935, **519**, 1; *A.*, 1134.

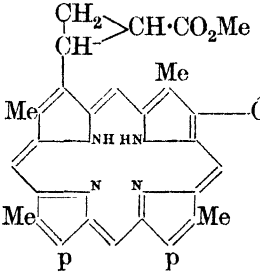
[12] The nomenclature is rather confusing: " Deoxo " here implies the reduction of the keto-group at C_9; " oxo " in oxophylloerythrin, that an acetyl group is present instead of ethyl at C_2.

(at C_6) of oxopyrroporphyrin.[13] Hence the substituent already present at C_2 is acetyl.

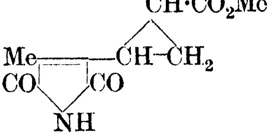
The formula of the oxoporphyrins is typified by (XXXVIII) :



(XXXVIII.)



(XXXIX.)



(XL.)

R = CO_2Me, Oxophæoporphyrin a_5.
R = H, Oxophylloerythrin.

The unsaturated side chain which gave rise to the acetyl group might be ethylidene or vinyl. This was settled by H. Fischer and H. Medick by use of the diazoacetic ester reaction.[14] Protoporphyrin, the metal-free porphyrin corresponding to hæmin, is known to contain two vinyl groups.[71] It reacted with diazoacetic ester at 100° with elimination of nitrogen to yield the corresponding di*cyclo*propane compound (XXXIX).[14] The absorption bands were shifted towards the blue region and the product no longer reacted with hydrobromic acid. Oxidation of (XXXIX) with chromic and sulphuric acids gave a mixture of hæmatic acid and the *cyclo*propane maleinimide (XL).

Methyl phæophorbide *a* also reacted with diazoacetic ester. The absorption bands were shifted slightly towards the blue region, but without alteration of the characteristic phorbide type. The product on isomerisation with hydriodic and acetic acids gave the corresponding porphyrin, the analysis of which agreed with the addition of a $>CH \cdot CO_2Me$ group. Pyrophæophorbide gave a similar compound, which could also be obtained by the pyrolysis of the methylphæophorbide product. Catalytic reduction and reoxidation of this yielded the porphyrin addition compound corresponding to phylloerythrin. Vigorous oxidation of this gave methylethylmaleinimide and the *cyclo*propane compound (XL) identical with that obtained from the addition compound of protoporphyrin. The same substance was obtained in bad yield by the direct oxidation of the diazoacetic ester adduct of pyrophæo phorbide. Chlorin *e* trimethyl ester also added diazoacetic ester

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[13] H. Fischer and J. Hasenkamp, *Annalen*, 1935, **519**, 42; *A.*, 1134.
[14] *Ibid.*, 1935, **517**, 245; *A.*, 871.

The significance of these results is increased by the fact that porphyrins with saturated side chains such as the hæmato- and meso-porphyrin of the hæmin series, and the phæoporphyrin a_5 and phylloerythrin of the chlorophyll series, do not react with diazoacetic ester.

The important fact therefore emerges that the nearest derivatives of chlorophyll contain the vinyl group in the same position as one of the vinyl groups of hæmin and the leaf and blood pigments therefore come into even closer relationship.

The recognition of the unsaturated side chain as a vinyl group has the advantage that its conversion into the acetyl group by the "oxo-reaction" can be interpreted simply as follows: [14]

$$>\!\text{CH:CH}_2 \xrightarrow{\text{HI}} >\!\text{CHI·CH}_3 \xrightarrow{\text{H}_2\text{O}} >\!\text{CH(OH)·CH}_3 \xrightarrow{\text{O}} >\!\text{CO·CH}_3$$

The mechanism which had previously been advanced to explain the formation of a carbonyl-containing side chain from an ethylidene or methylene group had been comparatively complicated.

A difficulty which remained was that, though the vinyl groups in hæmin add the elements of hydrogen bromide or water readily, this had not been observed in the chlorophyll series. H. Fischer and J. Hasenkamp [13] have, however, found that the vinyl groups of phæophorbide *a* add hydrogen bromide under the conditions which convert hæmin into hæmatoporphyrin. The hydrogen bromide adduct is unstable, but its methanolysis products have been isolated.

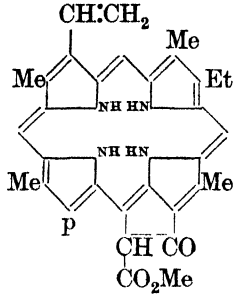
The assignment of one double bond in the side chains in place of the three of the earlier Fischer formula (XXXIII) was in harmony with the formation and properties of dihydrophæophorbide. This had been prepared by the hydrogenation of phæophorbide *a* in formic acid with one mole of hydrogen over Adams's catalyst.[15] It is phase-positive and yields an oxime; hence the carbonyl group has not been reduced. Preliminary experiments indicated that this and other dihydro-compounds gave a poor yield of "oxo-compounds." Re-examination of dihydrophæophorbide, carefully purified by the chromatographic method, showed that only phæoporphyrin a_5 and no oxoporphyrin was formed under the conditions of the oxo-reaction.[13] Hence the dihydro-compound carries an ethyl group in place of vinyl at C_2. It seems probable that the early discovery by J. B. Conant and J. F. Hyde [16] that phæophorbide *a* and chlorin *e*, but not porphyrins, could be reduced in aqueous solution by hydrogen over palladised asbestos, can also be explained as a reduction of the vinyl group.

[15] H. Fischer and E. Lakatos, *Annalen*, 1933, **506**, 123; *A.*, 1933, 1308.

[16] *J. Amer. Chem. Soc.*, 1930, **52**, 233; *A.*, 1930, 799.

These results led Fischer to propose formulæ for chlorophyll *a* based on the following for phæophorbide *a*.

(XLI*a*.)



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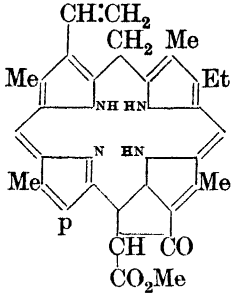

(XLI*b*.)

More recent modifications of these are dealt with later.

Allomerisation and the Phase Test.—When an alcoholic solution of chlorophyll is evaporated to dryness or allowed to stand, it is allomerised and loses its power of crystallisation.[17] This process was recognised as an oxidation by J. B. Conant,[18] who is responsible for much of our knowledge in this field. He showed that the oxidising agent was aerial oxygen and that two equivalents of O were utilised.[19] This was confirmed by H. Fischer,[20] who found that benzoquinone could bring about a similar change. Another dehydrogenating agent is potassium molybdicyanide.[21]

The "phase test" is the green ⟶ brown ⟶ green colour change brought about in chlorophyll derivatives by the addition of methyl-alcoholic potash (p. 367). This also was shown to involve an oxidation by two equivalents of aerial oxygen.[22] As has been stated, rapid saponification of phæophorbide *a* with boiling methyl-alcoholic potash yields chlorin *e* without oxidation, because the alcohol vapour protects the phorbide from the air. In phase-test saponification, the hydrolysis is slower and oxidation can proceed. Similar results were obtained by H. Fischer, O. Süs, and G. Klebs,[20] who found that the first colour change (green to brown) does not involve oxidation, which only occurs during the change back to green. Some chlorin *e* is normally formed during phase-test saponification, but it was found by J. B. Conant and W. W. Moyer[23] that this could be entirely prevented if ethyl or, better, *n*-propyl alcohol was used in place of methyl alcohol as a solvent. This is due to the ready absorption of oxygen by the solutions of alkali in the higher alcohols. Allomerised chlorophyll does not show a brown phase, but gives a green solution at once under phase-test conditions. These results show the correctness of Willstätter's view that the changes brought about by the phase test and allomerisation are essentially the same.

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[17] R. Willstätter and M. Utzinger, *Annalen*, 1911, **382**, 129; *A.*, 1911, i, 659.

[18] J. B. Conant, J. F. Hyde, W. W. Moyer, and E. M. Dietz, *J. Amer. Chem. Soc.*, 1931, **53**, 359; *A.*, 1931, 368.

[19] J. B. Conant, S. E. Kamerling, and C. C. Steele, *ibid.*, p. 1615; *A.*, 1931, 745.

[20] *Annalen*, 1931, **490**, 84; *A.*, 1931, 1431.

[21] J. B. Conant, E. M. Dietz, C. F. Bailey, and S. E. Kamerling, *J. Amer. Chem. Soc.*, 1931, **53**, 2382; *A.*, 1931, 1075.

[22] C. C. Steele, *ibid.*, p. 3171; *A.*, 1931, 1169. Compare ref. 19.

Willstätter[17] had shown that the principal product of phase-test saponification of phæophytin was an unstable chlorin, phytochlorin *g*. Conant and Moyer[23] found that the same mixture of unstable chlorins was formed by treatment of the phorbides and of chlorin *e* tri-ester under the conditions of the phase test. On standing in ether, these changed into two purplish-brown crystalline solids called phæopurpurin 7 and 18.[24] Phæopurpurin 7 was a monomethyl ester and yielded with diazomethane a trimethyl ester which was also formed directly from the unstable chlorins by the same reagent. When hydrolysed with hot methyl-alcoholic alkali, it lost the group $—CO·CO_2Me$, yielding chlorin *f* and potassium oxalate. This indicated that it contained an α-ketonic acid group. Chlorin *f*[25] is a dibasic acid which on treatment with hydrogen iodide and reoxidation yielded rhodoporphyrin, which was also formed directly from phæopurpurin 7 and alcoholic potash at 150°.[23] Pyrolysis of chlorin *f* yielded pyrroporphyrin (see scheme below).

Phæopurpurin 18, which contains one free and two masked carboxyl groups, is formed from the unstable chlorins by fission of carbon dioxide on standing in ether.[26] Its hydrolysis yielded a chlorin (tri-acid) apparently identical with Willstätter's chlorin *a* and called chlorin *p* 6 by Fischer. This regenerated phæopurpurin 18 on standing or by the action of heat. When heated alone or in solvents, phæopurpurin 18 yielded the curious green anhydride of rhodoporphyrin-γ-carboxylic acid,[27] and with alcoholic potash at 150°

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[23] *J. Amer. Chem. Soc.*, 1930, **52**, 3013; *A.*, 1930, 1299.

[24] These suffixes correspond with the acid numbers of the compounds. (See p. 366.)

[25] Probably identical with Willstätter's phytochlorin *f* ("Chlorophyll," p. 303), and named rhodochlorin by Fischer.

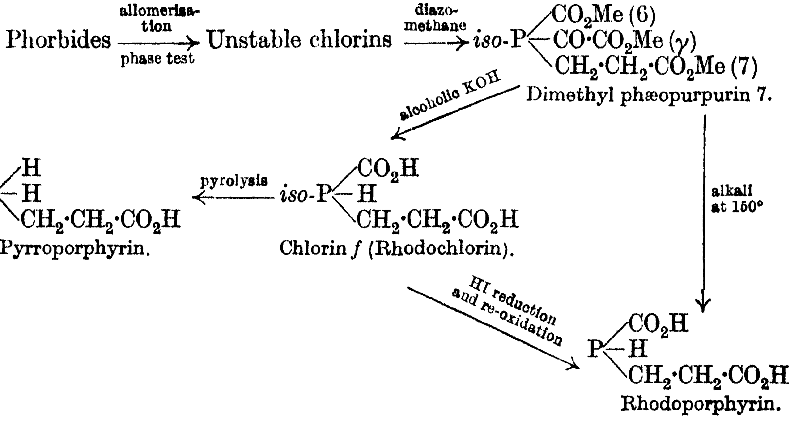
[26] E. M. Dietz and W. F. Ross, *J. Amer. Chem. Soc.*, 1934, **56**, 159; *A.*, 1934, 308. These authors point out that chlorin *a* and phæopurpurin 18 had been described by H. Malarski and L. Marchlewski in 1912 (*Biochem. Z.*, **42**, 219; *A.*, 1912, i, 641) under the names β-phyllotaonin and anhydro-β-phyllotaonin respectively.

[27] H. Fischer, W. Gottschaldt, and G. Klebs, *Annalen*, 1932, **498**, 194; *A.*, 1932, 1263.

rhodoporphyrin itself.[23] From these results, Conant concluded that both allomerisation and the phase test involve a change from the potential phylloporphyrin to the potential rhodoporphyrin structure.[18]

Fischer and Conant are in substantial agreement on the structures of the products of these reactions, though they differ as to the nature of the *iso*porphin–porphin change and the mechanism of allomerisation. It will be convenient to neglect the first difference for the moment and to write P for the main porphin unit of the chlorophyll porphyrins and *iso*-P for the corresponding unit of the phorbides, chlorins, and purpurins. [On this basis chlorin *e* (according to Fischer) is $iso\text{-P}\!\left<\begin{array}{l}CO_2H\ (6)\\ CH_2{\cdot}CO_2H\ (\gamma)\\ CH_2{\cdot}CH_2{\cdot}CO_2H\ (7)\end{array}\right.$ and rhodoporphyrin is $P\!\left<\begin{array}{l}CO_2H\ (6)\\ H\ (\gamma)\\ CH_2{\cdot}CH_2{\cdot}CO_2H\ (7).]\end{array}\right.$

Dimethylphæopurpurin 7 is recognised as the tri-ester of the γ-glyoxylic acid corresponding to chlorin *e*, and its transformations are illustrated below :[28]



The reactions of phæopurpurin 18, which contains one carbon atom less than phæopurpurin 7, are interpreted on p. 388.[18, 23, 26, 27]

The purpurins and the chlorins derived from them are here represented as containing the *iso*porphin structure, and hence, according to Fischer, a vinyl group on C_2. This is not fully proved, but is supported by a recent statement[29] that phæopurpurin 7, rhodochlorin, and chlorin *p* 6 all react with diazoacetic ester.

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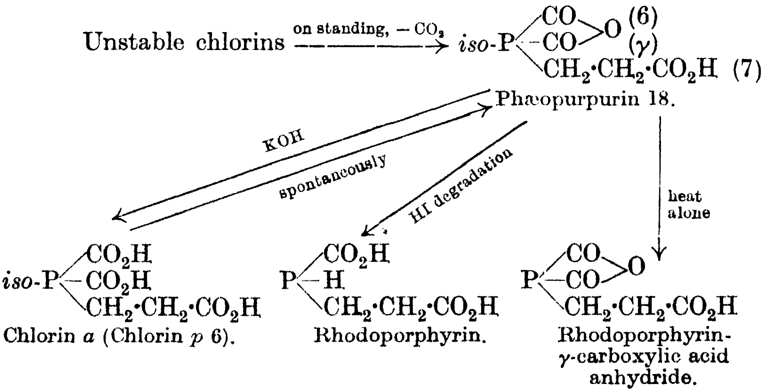
[28] Based on the scheme given in ref. 18.

[29] H. Fischer and A. Stern, *Annalen*, 1935, **520**, 88; *A.*, 1383.

The study of phæopurpurin 7 has opened up a new field for investigation. When the unstable chlorins prepared by the phase test or allomerisation are allowed to stand, phæopurpurin 7 is obtained as a monomethyl ester. The methyl group corresponds to that in phæophorbide *a* and chlorophyll *a*. When the compound is pyrolysed in boiling diphenyl, it yields, not chlorin *f*, but its monomethyl ester,[18] *i.e.*, the methyl group is not lost with the 10-carboxyl. This suggests that phæopurpurin 7 contains a carbomethoxy- (or similar) group at C_6; the suggestion, however, conflicts with the weight of evidence which places this group in other chlorophyll derivatives at C_{10}. Conant and Dietz[30] find that phæopurpurin 7 originates from an isomeric impurity in phæophorbide. The purest phæophorbides by the same treatment yield no phæopurpurin 7, but a monomethyl compound in which the carbomethoxy-group is at C_{10} as in the usual formulæ. These experiments suggest that the isomeric impurity with the abnormal position of the carbomethoxy-group corresponds to a second form of chlorophyll *a*. If this can be substantiated, it opens up interesting possibilities.



Fischer and his collaborators have made a thorough study of the allomerisation of chlorophyll derivatives by benzoquinone and by iodine, the general conclusion being that oxidation occurs at C_{10}. The following results are some of the most significant. If ethyl chlorophyllide is allomerised with benzoquinone in ethyl alcohol, and the product treated with hydrochloric acid in ether, crystalline ethyl 10-ethoxyphæophorbide is obtained.[31] This yields a dihydro-compound (presumably with reduction of the

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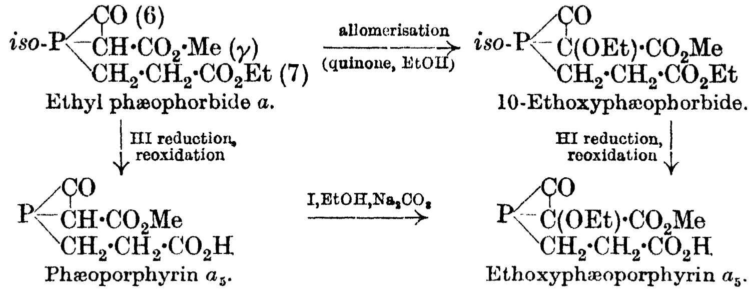
[30] *Nature*, 1933, **131**, 131; *J. Amer. Chem. Soc.*, 1933, **55**, 839; *A.*, 1933, 287, 403.

[31] H. Fischer and J. Riedmair, *Annalen*, 1933, **506**, 107; *A.*, 1933, 1308; cf. H. Fischer, L. Filser, and E. Plötz, *ibid.*, 1932, **495**, 1; *A.*, 1932, 756.

2-vinyl group) and, when it is fully reduced with hydrogen iodide [31] or catalytically [32] and reoxidised, gives ethoxyphæoporphyrin a_5 (phæoporphyrin a_6). The structure of this was known from the work of H. Fischer and J. Heckmaier,[33] who had obtained it by the oxidation of phæoporphyrin a_5 (dimethyl ester) with iodine in ethyl alcohol in the presence of sodium carbonate. On the basis of Fischer's formulæ, these results can be summarised by the scheme :



Ethyl phæophorbide *a*.

10-Ethoxyphæophorbide.

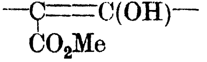
Phæoporphyrin a_5.

Ethoxyphæoporphyrin a_5.

Methyl phæophorbide *a* can be oxidised similarly with iodine in the presence of sodium acetate to methyl 10-hydroxyphæophorbide.[33] The acetyl compound of this contains the phorbide (*iso*porphin) ring structure intact and gives the " oxo-reaction." When the free 10-hydroxy-compound is hydrolysed with caustic soda, the isocyclic ring is broken and unstable chlorins are formed, which with diazomethane yield dimethylphæopurpurin 7.[34]

Different mechanisms of allomerisation have been proposed by Fischer and by Conant. The former suggested that the first process was dehydrogenation with the formation of a double bond between C_γ and C_{10}, this being followed by the addition of water or alcohol.[35] Conant's view was that allomerisation consisted in the dehydrogenation of a secondary alcohol group at C_{10}. Further comment is unnecessary in view of the unsettled state of the subject.

According to Fischer, the brown phase of chlorophyll derivatives, the formation of which does not involve oxidation, is connected with the formation of an enol at C_9 :[36]



$-\underset{CO_2Me}{\overset{10}{C}}{=\!=}\overset{9}{C}(OH)-$

R. Kuhn

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[32] H. Fischer, E. Lakatos, and J. Schnell, *Annalen*, 1934, **509**, 201 ; *A.*, 1934, 666.

[33] *Ibid.*, 1934, **508**, 250 ; *A.*, 1934, 420.

[34] H. Fischer, J. Heckmaier, and T. Scherer, *ibid.*, 1934, **510**, 169 ; *A.*, 1934, 785.

[35] This has been altered in a recent paper by H. Fischer and A. Stern (*ibid.*, 1935, **519**, 63 ; *A.*, 1134) to explain measurements of optical activity, but it is doubtful if the alteration is necessary.

[36] H. Fischer and H. Siebel, *ibid.*, 1932, **499**, 84 ; *A.*, 1932, 1263.

has suggested that an enolisation of the 10-carbomethoxy-group occurs.[37] The lengthening of the conjugated chain so obtained causes the red absorption band to move into the infra-red region, causing a lightening of the visible colour (green ⟶ yellow-brown).

Fine Structure of Chlorophyll a.—Considerable light has been thrown on this difficult subject by the application of three physical methods. It has long been known that porphyrins have multi-banded absorption spectra which may be used for their identification. J. B. Conant and S. E. Kamerling[38] have now found that at the temperature of liquid air the porphyrins show a unique spectrum of narrow bands in the visible region. The green derivatives of chlorophyll (phorbides, chlorins) have wider bands in the absorption spectra and are intermediate between most organic colouring matters and the porphyrins. The relationship between the visible spectra of porphyrins and the phorbides (or chlorins) resembles that between the ultra-violet spectra of benzene and *cyclo*hexadiene. This suggests strongly that chlorophyll derivatives contain the dihydroporphin ring.

Evidence pointing in the same direction has come from a study of the basicity of the four pyrrole-like rings in phorbides, chlorins, and porphyrins.[39] Willstätter's method of acid fractionation was based on the variation in basicity of chlorophyll derivatives and he had obtained evidence of the greater basicity of two of the nitrogen atoms by the isolation of dihydrochlorides. Conant and his collaborators measured the basicity by potentiometric titrations with perchloric acid in glacial acetic acid, using a chloranil electrode.[40] The derivatives of chlorophyll were compared with substituted pyrroles of known constitution. The porphyrins were found to contain two relatively strongly basic groups, presumably of the pyrrolenine type (XLII), and one very weakly basic group of the pyrrole (XLIII) or *iso*pyrrole (XLIV) type. The second weakly basic group could not be detected by the method. The phorbides contained one relatively strong and one very weak basic group and a group intermediate in strength. The chlorins resembled the phorbides except that the intermediate group was rather more basic. These facts are compatible with the green chlorophyll derivatives containing one pyrrolenine ring, two pyrrole or *iso*-pyrrole rings, and a dihydropyrrole nucleus of type (XLV).

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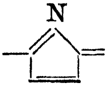
[37] R. Kuhn, P. J. Drumm, M. Hoffer, and E. F. Moller, *Ber.*, 1932, **65**, [*B*], 1785; *A.*, 1933, 52.

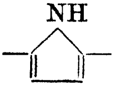
[38] *J. Amer. Chem. Soc.*, 1931, **53**, 3522; *A.*, 1931, 1310.

[39] J. B. Conant, B. F. Chow, and E. M. Dietz, *ibid.*, 1934, **56**, 2185; *A.*, 1934, 1371.

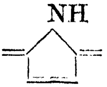
[40] Cf. J. B. Conant and T. H. Werner, *ibid.*, 1930, **52**, 449; *A.*, 1931, 40; J. B. Conant and B. F. Chow, *ibid.*, 1933, **55**, 3745; *A.*, 1933, 1121.



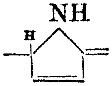
(XLII.)



(XLIII.)



(XLIV.)



(XLV.)

It had long been thought that chlorophyll and its derivatives were optically inactive; [41] the leuco-compounds showed no activity and the intense colour had prevented an examination of the pigments themselves. In 1933, A. Stoll and E. Wiedemann [42] overcame the experimental difficulties and showed that chlorophyll *a* and *b* were both lævorotatory with $[\alpha]^{25°}_{720}$ = about $-265°$. The activity might have come from the phytyl group, as phytyl alcohol is optically active before distillation,[43] but this was shown to be incorrect, since the phytyl- and magnesium-free phorbides of the *a* and *b* series also were active.[42] Stoll and Wiedemann state that chlorophylls, methyl phæophorbides, and phæophorbides (*a* and *b*) all racemise in acetone or methyl-alcoholic solution and that old samples of crystalline methyl phæophorbides are inactive. H. Fischer and A. Stern, using white light, have confirmed the optical activity but not the ease of racemisation. They state that both solutions and solids are optically stable.[44, 45] The following substances, *inter alia*, were found to be active : pyrophæophorbide *a*, chlorophyllides, 10-ethoxyphæophorbide, rhodochlorin, chlorin *p* 6 (tri-ester), and dimethylphæopurpurin 7, all being lævorotatory except the last two. The activity survived allomerisation, the phase test, and conversion of the active compounds into their metallic derivatives. On the other hand, all the porphyrins derived from these substances and those from hæmin (and also blood hæmin itself) are optically inactive. The only known active porphyrin is uroporphyrin from mussel-shells, and in this the active centres are very probably different from those of the chlorophyll derivatives, being located in succinic acid side chains.[45]

As far as the chlorophyll series is concerned, the activity is undoubtedly associated with the *iso*porphin structure. The fact that phæophorbide was not racemised on conversion into pyrophæophorbide showed that C_{10} was not the active centre (or not the only active centre). As this was the only asymmetric carbon atom in Fischer's current formulæ (XLI*a* and *b*), these became invalid. Fischer and Stern first suggested[44] that the γ-carbon atom carried a hydrogen atom and was an active centre, but abandoned this idea in view of the activity of rhodochlorin (chlorin *f*), in which this carbon atom must be of the type —CH= or —CH_2—. They point out that asymmetric carbon atoms can only appear by the formation of a dihydroporphin system and that reduction must occur on one of the pyrrole rings and not at the methene bridges or by addition of hydrogen to two nitrogen atoms.[45] Of the various possibilities, Fischer now prefers formula (XLVI) for chlorophyll *a*. In this, ring III is tentatively selected as the reduced ring and hence carbon atoms 5 and 6 as the asymmetric centres.[45] This formula (or some near modification)[46] can explain all the more recent facts and is by far the most satisfactory of those in the field.

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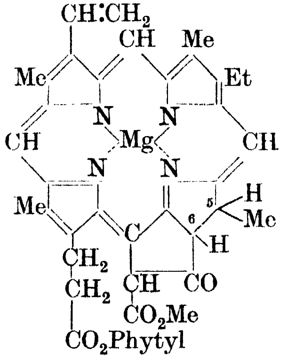
[41] See, *e.g.*, H. Fischer and H. Siebel, *Annalen*, 1932, **499**, 94; *A.*, 1932, 1263.

[42] *Helv. Chim. Acta*, 1933, **16**, 307; *A.*, 1933, 515.

[43] R. Willstätter and F. Hocheder, *Annalen*, 1907, **354**, 248; R. Willstätter, E. W. Mayer, and E. Hüni, *ibid.*, 1911, **378**, 84; *A.*, 1907, i, 784; 1911, i, 144.

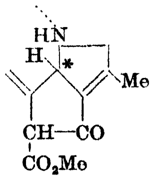
[44] *Ibid.*, 1935, **519**, 58; *A.*, 1134.

[45] *Ibid.*, **520**, 88; *A.*, 1383.



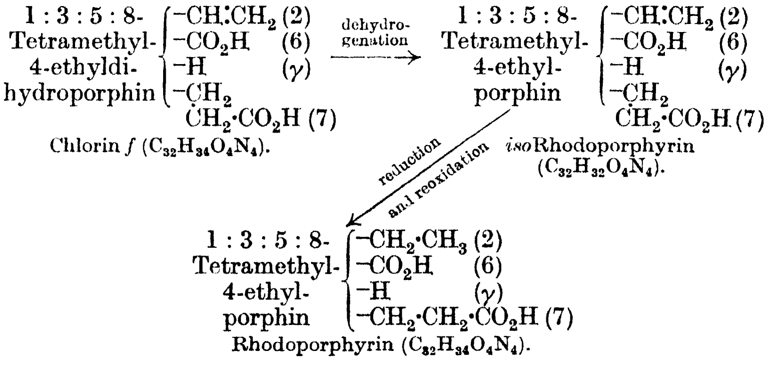
(XLVI.)

[46] It appears to the Reporter that a slight modification of (XLVI) in which the two extra hydrogens are placed on a (C=N) bond of one of the pyrrole rings (probably ring III) would accommodate the physical results better. The partial formula is shown in (XLVI*a*), the rest of the molecule being the same as in (XLVI). Formula (XLVI*a*) contains an interrupted conjugated chain, in place of the continuous conjugation of the porphyrins and (XLVI), to account for the considerable change in absorption spectrum; and also the dihydropyrrole ring, as suggested by Conant. Apart from C_{10} it contains only one asymmetric carbon atom (starred). The substance (XLVI) can give rise to two inactive and resolvable (*cis*- and *trans*-) forms according to the arrangement of the substituents at C_5 and C_6. No such isomerides appear to be known.



(XLVI*a*.)

The formulæ of Conant and Stoll are not very different from the above with regard to the *iso*porphin system. If it be accepted that the true porphyrins from chlorophyll contain an ethyl group at C_2, and the *iso*porphyrins (phorbides and chlorins) a vinyl group, then we can reconcile the view that the porphyrins and *iso*porphyrins are isomeric and at the same level of reduction (Fischer) with the view, advanced by Conant from the physical results and also held by Stoll, that the *iso*porphyrins contain a dihydroporphin structure. In this connection it is of interest that Conant[47] was able to dehydrogenate chlorin *f* to a porphyrin, *iso*rhodoporphyrin (called ψ-verdoporphyrin by Fischer). This could be converted into rhodoporphyrin by reduction with hydrogen iodide and reoxidation, also by mineral acids under certain conditions, but not by mild treatment.[47,48] Rhodoporphyrin is known to carry an ethyl group at C_2 and the latest work shows that chlorin *f* carries a vinyl group. On this basis *iso*rhodoporphyrin also should have a vinyl group at C_2 and should contain two hydrogen atoms less than rhodoporphyrin.[50] This is in keeping with the results of catalytic hydrogenation[49,48] and with other experiments briefly mentioned in Fischer's recent paper.[45] If this can be confirmed, one of the remaining difficulties of the subject will disappear and the changes can be represented as follows :[51]



1 : 3 : 5 : 8-Tetramethyl-4-ethyldihydroporphin $\begin{cases} -CH{:}CH_2 \ (2) \\ -CO_2H \ (6) \\ -H \ (\gamma) \\ -CH_2{\cdot}CH_2{\cdot}CO_2H \ (7) \end{cases}$ $\xrightarrow{\text{dehydrogenation}}$ 1 : 3 : 5 : 8-Tetramethyl-4-ethylporphin $\begin{cases} -CH{:}CH_2 \ (2) \\ -CO_2H \ (6) \\ -H \ (\gamma) \\ -CH_2{\cdot}CH_2{\cdot}CO_2H \ (7) \end{cases}$

Chlorin *f* ($C_{32}H_{34}O_4N_4$).

*iso*Rhodoporphyrin ($C_{32}H_{32}O_4N_4$).

reduction and reoxidation

1 : 3 : 5 : 8-Tetramethyl-4-ethylporphin $\begin{cases} -CH_2{\cdot}CH_3 \ (2) \\ -CO_2H \ (6) \\ -H \ (\gamma) \\ -CH_2{\cdot}CH_2{\cdot}CO_2H \ (7) \end{cases}$

Rhodoporphyrin ($C_{32}H_{34}O_4N_4$).

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[47] J. B. Conant and C. F. Bailey, *J. Amer. Chem. Soc.*, 1933, **55**, 795; *A.*, 1933, 403.

[48] E. M. Dietz and T. H. Werner, *ibid.*, 1934, **56**, 2180; *A.*, 1934, 1371.

[49] H. Fischer and E. Lakatos, *Annalen*, 1933, **506**, 123; *A.*, 1933, 1308.

[50] Comparison of the absorption spectra of these substances, according to A. Stern and H. Wenderlein, supports the idea that they are not isomeric (*Z. physikal. Chem.*, 1934, **170**, 337; *A.*, 1935, 10).

[51] Dietz and Werner (ref. 48) summarise the position from the other point of view (namely, that the true and the *iso*-porphyrins are isomeric and that the nucleus of chlorophyll is a dihydro*iso*porphyrin), which does not take into account the unsaturated side chain at C_2.

On this basis the term *iso*porphyrin ceases to have any special significance, beyond implying a 2-vinyldihydroporphyrin.

Partial Synthesis of Chlorophyll a.—The synthesis of phylloerythrin by Fischer leaves only four main gaps in the complete synthesis of chlorophyll *a*. These are (i) the introduction of a carbomethoxy-group, (ii) the conversion of the porphin into the *iso*porphin system, (iii) the introduction of the phytyl group, and (iv) of the magnesium atom. The last two stages have been achieved by Fischer.

R. Willstätter and L. Forsén [52] introduced magnesium into phæophytin and other chlorophyll derivatives by the action of the Grignard reagent, a method also used by A. Stoll and E. Wiedemann.[53] Fischer and his collaborators used the product (RO·MgBr) of the decomposition of the Grignard reagent with an alcohol, in order to avoid secondary reactions with carboxy- or carbomethoxy-groups,[54] but his latest paper on the subject [55] makes it doubtful if any of these processes are satisfactory for the preparation of phase-positive material. The method finally found satisfactory is the interaction of the phorbide with a compound of the RO·MgBr type in the presence of pyridine and an excess of magnesium.[55] By this process pure phase-positive chlorophyllide *a* can be prepared from methyl phæophorbide *a* more readily than by the chlorophyllase reaction. This confirms the relationship between the two substances.

The esterification of the propionic acid group by phytyl alcohol was achieved by R. Willstätter and A. Stoll [56] by a biological method. H. Fischer and W. Schmidt [57] have successfully applied Einhorn's method.[58] A solution of phæophorbide *a* in pyridine on treatment with phytyl alcohol and carbonyl chloride gave phæophytin *a* indistinguishable from the natural product. When hydrolysed in the presence of chlorophyllase, it regenerated phæophorbide *a*; hence there was no replacement of methyl by phytyl at C_{10}. Other esters of phæophorbide were prepared by this process and the interesting observation was made that the enzymic action of chlorophyllase is relatively but not absolutely specific; *e.g.*, it catalysed the hydrolysis of geranyl and cetyl phæophorbides, but not that of the methyl and the bornyl ester.[58]

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[52] *Annalen*, 1913, **396**, 180; *A.*, 1913, i, 499.

[53] *Naturwiss.*, 1932, **20**, 630.

[54] H. Fischer and M. Dürr, *Annalen*, 1933, **501**, 107; *A.*, 1933, 515; H. Fischer and J. Riedmair, *ibid.*, 1933, **506**, 118; *A.*, 1933, 1308.

[55] H. Fischer and G. Spielberger, *ibid.*, 1934, **510**, 156; *A.*, 1934, 785.

[56] *Ibid.*, 1911, **380**, 148; *A.*, 1911, i, 391.

[57] *Ibid.*, 1935, **519**, 244; *A.*, 1382.

[58] *Ibid.*, 1898, **301**, 95; *A.*, 1898, i, 577.

Phæoporphyrin a_5 has not yet been synthesised [59] and it appears that the porphin ⟶ *iso*porphin conversion will be difficult. Synthesis from 2-de-ethylporphyrins, followed by introduction of the vinyl group, may be necessary.

Chlorophyll b.—The study of this compound is not so well advanced as that of chlorophyll *a*, and only a brief summary of progress will be given here. As has already been stated, chlorophylls *a* and *b* are very similar in general properties, and phyllides and phorbides of the *b* series can be prepared by the usual methods. The formula proposed by Willstätter for chlorophyll *b* ($C_{55}H_{70}O_6N_4Mg$) is generally accepted. This contains one more atom of oxygen and two less of hydrogen than that of chlorophyll *a*. Drastic alkaline degradation of chlorophyll *b* gives pyrro-, rhodo-, and phyllo-porphyrins, but in worse yield than in the *a* series;[60] hence the essential arrangement of the substituents is the same. Phæophorbide *b* on complete reduction with hydrogen iodide yielded hæmopyrrole and hæmopyrrolecarboxylic acid.[61] Willstätter showed that phæophorbide *b* is converted by rapid hydrolysis with hot alkali into rhodin *g*, which is a tribasic acid containing 7 atoms of oxygen and corresponds to chlorin *e* of the *a* series. The extra oxygen atom of the *b* series was first proved by Conant [62] to be located in a carbonyl group by the preparation of a semicarbazone from phæophorbide *b*. This was shown independently by O. Warburg, who converted phæophorbide *b* into phæoporphyrin b_6 (corresponding to phæoporphin a_5) by hydrogen iodide, and prepared an oxime from this.[63] Fischer and his collaborators also have obtained a monoxime from rhodin *g* [64] and one from phæophorbide *b*.[65] The porphyrins obtained by hydrogen iodide degradation of phæophorbide *b* and rhodin *g* showed reactions parallel to those of the compounds of the *a* series; which indicated that a carbocyclic ring containing a *ψ*-acidic keto-group was also present in phæophorbide *b*.[65, 66] In 1934, A. Stoll and E. Wiedemann prepared a dioxime of methyl phæophorbide *b* and thus conclusively proved the presence of two carbonyl groups.

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[59] Cf. H. Fischer and T. Schorer, *Annalen*, 1935, **519**, 236; *A.*, 1382.

[60] Willstätter, "Chlorophyll," p. 334; cf. A. Treibs and E. Wiedemann, *Annalen*, 1929, **471**, 146; *A.*, 1929, 941.

[61] H. Fischer, A. Merka, and E. Plötz, *ibid.*, 1930, **478**, 299; *A.*, 1930, 620.

[62] J. B. Conant, E. M. Dietz, and T. H. Werner, *J. Amer. Chem. Soc.*, 1931, **53**, 4436; *A.*, 1932, 174.

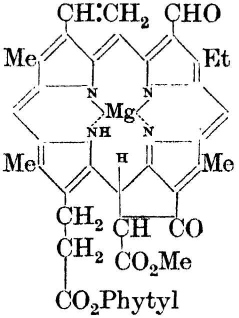
[63] *Biochem. Z.*, 1931, **235**, 1; 1932, **244**, 9; *A.*, 1931, 661.

[64] H. Fischer, F. Broich, S. Breitner, and L. Nüssler, *Annalen*, 1932, **498**, 228; *A.*, 1932, 1263.

[65] H. Fischer, S. Breitner, A. Hendschel, and L. Nüssler, *ibid.*, 1933, **503**, 1; *A.*, 1933, 839; cf. A. Stoll and E. Wiedemann, *Helv. Chim. Acta*, 1932, **15**, 1132; *A.*, 1932, 1265.

[66] H. Fischer, A. Hendschel, and L. Nüssler, *Annalen*, 1933, **506**, 83; *A.*, 1933, 1173; H. Fischer and S. Breitner, *ibid.*, 1934, **510**, 183; **511**, 183; *A.*, 1934, 785, 907.

The compounds of the *b* series therefore contain one carbonyl group in place of a methylene group of the *a* series. Conant first placed the additional carbonyl group as a ketonic bridge (at C_β) and Fischer put it in the propionic acid side chain (at C_7). Subsequently Fischer showed that it was present as a nuclear *aldehydo*-group on C_3.[67] Rhodin *g* trimethyl ester was degraded to 3-demethyldeoxophylloerythrin, the structure of which was proved by synthesis.[68] These results are embodied in the formula (XLVII) of H. Fischer and A. Stern,[69] which accommodates the optical activity of chlorophyll *b* and phæophorbide *b* discovered by A. Stoll and E. Wiedemann.[70] This is the most recent formula proposed by Fischer, but it would presumably now be modified with respect to the position of the two " extra " hydrogen atoms so as to come into line with formula (XLVI) for chlorophyll *a*. The presence of the vinyl group at C_2 is inferred by analogy, but has not been proved.



(XLVII.)

There now appears to be no justification for the supposition that chlorophyll *a* and *b* are readily interconvertible either in the plant or in the laboratory.[71]

Other Natural Porphyrin Derivatives.

Bacteriochlorophyll.—Some bacteria have the power of assimilating carbon dioxide and recent investigations have shown that they contain a pigment closely resembling chlorophyll. K. Noack and E. Schneider [72] first isolated the pigment of certain red sulphur or purpurbacteria of this type. They found that this compound, bacteriochlorophyll, contained magnesium removable by acids to give a substance resembling phæophytin. Two carboxyl groups were found to be present, one esterified by methyl, the other by phytyl or a similar alcohol,[73] and various derivatives were prepared. Noack and Schneider considered that two pigments were present, of which the one in larger amount resembled chlorophyll *b* and contained 6 atoms of oxygen in the molecule. H. Fischer and J. Hasenkamp [74] investigated the same (or a similar) substance, isolated by H. Gaffron from pure cultures of *Thiocystis violacea.* They found that the predominating pigment belonged to the *a* series and had an absorption spectrum of the "oxo"-type (see p. 381). The crystalline bacterio-methyl phæophorbide *a* prepared from it gave, on treatment with hydrogen iodide, two porphyrins, one of which was identical with oxophæoporphyrin a_5 ester. From this result the sixth oxygen atom was placed in an acetyl group on C_2. Fischer's formula [75] for bacterio-methyl phæophorbide *a* is (XLVIII), but the fine structure would presumably now be modified to agree with that of the last formula for chlorophyll *a* itself (XLVI). On Fischer's formulation, this substance and the two chlorophylls are all structurally derived from hæmin by comparatively simple processes of oxidation or reduction (the ester groups and central metal being neglected) :

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[67] H. Fischer, A. Hendschel, and L. Nüssler, *Annalen*, 1935, **516**, 61; *A.*, 530.

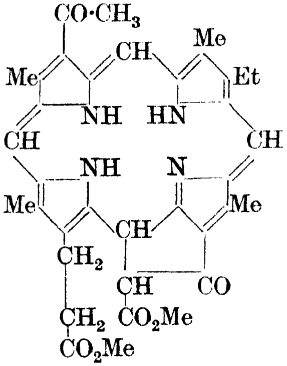
[68] H. Fischer and W. Rose, *ibid.*, 1935, **519**, 1; *A.*, 1134.

[69] *Ibid.*, p. 58; *A.*, 1134.

[70] *Helv. Chim. Acta*, 1933, **16**, 307; *A.*, 1933, 515.

[71] A. Stoll and E. Wiedemann, *Naturwiss.*, 1932, **20**, 889; *A.*, 1933, 167.

[72] *Ibid.*, 1933, **21**, 835; *A.*, 1934, 112.



(XLVIII.)

Substance.	Substituent at				
	C_2.	C_3.	C_4.	C_6.	C_7.
Hæmin	$CH{:}CH_2$	CH_3	$CH{:}CH_2$	$CH_2{\cdot}CH_2{\cdot}CO_2H$	$CH_2{\cdot}CH_2{\cdot}CO_2H$
Chlorophyll *a*......	,,	,,	C_2H_5	$CO{\cdot}\dot{C}H{\cdot}CO_2H$ *	,,
Chlorophyll *b*......	,,	CHO	,,	,,	,,
Bacterio-chlorophyll	$CO{\cdot}CH_3$	CH_3	,,	,,	,,

* Cyclised on to C_γ.

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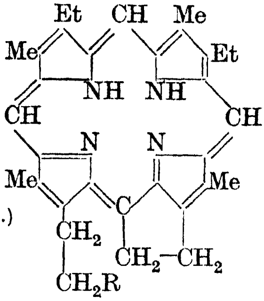
[73] E. Schneider, *Z. physiol. Chem.*, 1934, **226**, 221; *A.*, 1934, 1265.

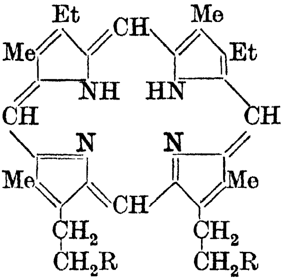
[74] *Annalen*, 1935, **515**, 148; *A.*, 362.

[75] H. Fischer and J. Hasenkamp, *ibid.*, 1935, **519**, 42; *A.*, 1134.

Porphyrins in Minerals.—A. Treibs has made an interesting study of the occurrence of porphyrins in a number of minerals. In 1934, from the bitumen of an oil shale from the Karwendel Mountains, he isolated two porphyrins,[76] deoxophylloerythrin (XLIX, R = CO_2H), and the decarboxylated compound, deoxophylloerythro-ætioporphyrin (XLIX, R = H).



(XLIX.)



(L.)

The structure of the first was known, that of the latter was proved shortly afterwards by synthesis.[77] Porphyrins were next found in other shales, in petroleums [78, 79] (from Galicia, Trinidad, etc.), in asphalts [78] (Trinidad, Dead Sea, etc.), in phosphorites,[79] and in many coals.[79, 80] Mineral waxes appeared to contain very little porphyrin.[78] The richest sources were Trinidad oil (which contained about 0·04% of total porphyrin) and particularly a bituminous marl from Switzerland (0·4%).[79] These quantities are astonishingly high when compared with the chlorophyll content of dried leaves (0·8%).

The mineral was extracted successively with acetic acid and chloroform, and the extract treated at 50° with hydrobromic and acetic acids.[76] The porphyrins were finally purified by acid fractionation. Besides the two compounds mentioned above, which are derivatives of chlorophyll, Treibs has identified meso-ætioporphyrin (L, R = H) and mesoporphyrin (L, R = CO_2H) of the hæmin series.[78] Coproporphyrin was detected in guano.[79] The chlorophyll porphyrins are always present in greater amount than those from hæmin, and the decarboxylated compounds predominate over the free acids. The deoxophylloerythrin and the derived ætioporphyrin from the Swiss marl occur naturally combined with vanadium in the centre of the large ring, as compounds of the type $>VO$, $>VO_2$ or $>V(OH)_2$.[79] It appears probable that the vanadium enters the complex as a result of a secondary reaction. A stable ferrous complex also has been detected.[79] There can be little doubt that chlorophyll and hæmin are the parent substances from which these porphyrins are formed by geological processes. The purity of the products makes it unlikely that there has been ring opening and resynthesis. The production of vanadyl deoxophylloerythro-ætioporphyrin from chlorophyll *a* involves the stages : (i) replacement of magnesium by vanadium, (ii) elimination of the labile carbomethoxy-group at C_{10} ; (iii) conversion into the porphyrin system, and (iv) decarboxylation at C_7. The decomposition of phæophytin to deoxophylloerythro-ætioporphyrin in petroleum at 360° has been reproduced artificially.

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[76] *Annalen*, 1934, **509**, 103; *A.*, 1934, 387.
[77] H. Fischer and H. J. Hofmann, *ibid.*, 1935, **517**, 274; *A.*, 871.
[78] A. Treibs, *ibid.*, 1934, **510**, 42; *A.*, 1934, 629.
[79] *Idem*, *ibid.*, 1935, **517**, 172; *A.*, 727.
[80] *Idem*, *ibid.*, 1935, **520**, 144; *A.*, 1347.

A number of interesting deductions have been drawn by Treibs. The results prove that plants play a major part in the formation of petroleum. The rôle of animals appears less important. The decompositions which they undergo must be comparatively mild; this agrees with the discovery of optical activity, and recently of œstrogenic properties, in petroleums. Moreover the two carboxylated porphyrins, mentioned above, act as recorders of the maximum temperature to which the oil has been subjected, for direct experiment shows that mesoporphyrin is decarboxylated by a week's heating at 240°. Treibs estimates that oils or minerals containing acid porphyrins cannot have been subjected to a temperature of more than 200° at any stage during their formation.

It has been necessary to omit a great deal of interesting material in compiling this Report on the porphyrin field. As usual, the more complete topics have been discussed.

R. P. L.

E. H. FARMER.
E. L. HIRST.
R. P. LINSTEAD.
S. PEAT.
F. S. SPRING.
E. E. TURNER.

BIOCHEMISTRY

THE year has seen steady progress in many directions, and it is a matter for regret that limitations of space forbid mention of more than a relatively small number of the advances which have been made. Selection has not been easy; the inclusion of certain subjects was obvious, but in other cases the choice between inclusion and omission was necessarily decided rather by the personal interests of the Reporter than by the relative importance of the subjects, which could not readily be distinguished. Even in the subjects chosen for review, much interesting and meritorious work has perforce received no direct reference.

Among the vitamins, B_1 has come into prominence since the publication, at the beginning of the year, of its probable structure; the presence of a pyrimidine derivative in the molecule, together with a number of scattered references to the occurrence and importance of pyrimidines, suggests that in the near future we may expect a great increase in the number of publications dealing with these substances. Flavin chemistry has received a good deal of attention, and it seems that the structure of lactoflavin is settled, though that of its phosphoric ester, the prosthetic group of the Warburg and Christian yellow enzyme, is still a matter for research with respect to the position of the ester linkage. It seems probable that calciferol, which is no longer alone as an artificial anti-rachitic substance, is not identical with the vitamin D present in fish-liver oils. Since vitamin E is now known to be an alcohol, we may confidently expect its complete isolation very soon.

The male sex-hormone now resembles oestrone in that its characteristic activity is exhibited by a number of related compounds; although the most active of them, testosterone, is regarded as the true hormone, one wonders whether that is a final verdict. The corpus luteum hormone, whose structure bears a remarkable resemblance to that of testosterone, still appears to be specific.

The process of the conversion of carbohydrate into lactic acid in muscle (or alcohol in yeast) is emerging as a series of reactions in which, at two important points, phosphate is received from or transferred to the nucleotide co-enzyme of the system. Phosphocreatine is not essential to the system, but appears to be intimately connected with it in muscle, in a manner not yet clear.

The synthesis of glutathione is an important achievement in the field of organic biochemistry and finally settles the constitution of this substance, whose functions in the living cell are gradually being elucidated.

In the field of intermediate metabolism the most important advance of the year is undoubtedly the demonstration that the theory of β-oxidation is unable to explain the known facts concerning the oxidation of fatty acids.

Chemotherapy is advancing in many directions, and the examples chosen are merely illustrative of the way in which synthetic substances may supplement or replace naturally occurring drugs and of the applications of biochemistry in determining the mode of action of drugs or even of initiating a new form of therapeutic treatment.

In the plant biochemistry section considerable space has again been devoted this year to growth-regulating substances. The rapid extension of our knowledge in this field seems to demand a continuation of the Report of last year, in conjunction with which the following section should be read. The nature of frost resistance in plants has assumed academic as well as practical importance, and in view of the fact that no reference has been made to this subject in these Reports for some years a review of the present position is included. The section relating to the biochemistry of moulds covers the past two years.

1. Animal Biochemistry.

Vitamins.

Vitamin B_1 (Aneurin).[1]—It is now generally admitted that the various crystalline preparations of vitamin B_1 hydrochloride are substantially identical and that the substance has the empirical formula $C_{12}H_{18}ON_4Cl_2S$. As a result of a series of investigations by R. R. Williams and his co-workers considerable progress has been made in the elucidation of the structure of the vitamin. When the hydrochloride is kept at room temperature in contact with a solution of sodium sulphite containing sufficient excess of sulphurous acid to bring it to p_H 4—5, it undergoes fission, giving two products, C_6H_9ONS (A) and $C_6H_9O_3N_3S$ (B), in 97% yield.[2] The product A is an oily base, giving crystalline salts; it contains a hydroxyl group and on oxidation with nitric acid yields an acid, $C_5H_5O_2NS$, identical with that previously obtained by A. Windaus, R. Tschesche, and

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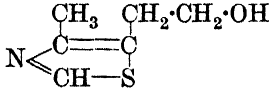
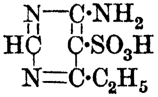
[1] B. C. P. Jansen, *Nature*, 1935, **136**, 259.

[2] R. R. Williams, *J. Amer. Chem. Soc.*, 1935, **57**, 229; *A.*, 504; R. R. Williams, R. E. Watermann, J. C. Keresztesy, and E. R. Buchman, *ibid.*, p. 536; *A.*, 668.

R. Grewe [3] by direct oxidation of the vitamin.[4] This acid has been identified as 4-methylthiazole-5-carboxylic acid,[5, 6] and the basic product of the sulphite cleavage has been proved by synthesis to be 4-methyl-5-β-hydroxyethylthiazole (I).[5] To product B—the acidic product of the sulphite cleavage—is provisionally allocated the structure (II).[2, 7] The evidence here is of a more slender nature, but the substance has the properties of a 6-aminopyrimidine-sulphonic acid : the disposition of the sulpho- and the ethyl group is arbitrary and it is of course possible that the ethyl group should be replaced by two methyl groups.

(I.)

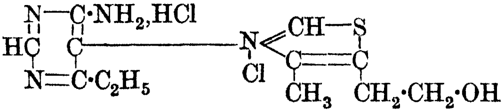




(II.)

The sulphite cleavage of the vitamin, taken in conjunction with its other properties, led R. R. Williams [2] to propose a tentative formula (III) for vitamin B_1 hydrochloride.

(III.)*



This formula contains a quaternary nitrogen atom and, although the evidence from electrometric titration curves is conflicting,[8, 9] R. R. Williams and A. E. Ruehle [10] consider that their results by this method indicate the presence of such an atom.

Early this year R. A. Peters [11] reported that aqueous solutions of vitamin B_1 acquired a blue fluorescence on oxidation, and R. Kuhn, Th. Wagner-Jauregg, F. W. van Klaveren, and H. Vetter [12] later isolated from yeast a yellow basic substance, thiochrome, $C_{12}H_{14}ON_4S$, exhibiting an intense blue fluorescence in neutral or alkaline solution. The close relationship in empirical formula between thiochrome and the vitamin suggested that the former might be the substance responsible for the fluorescence noted by Peters and might arise from vitamin B_1 present in the yeast. The preparation of thiochrome from vitamin B_1 by oxidation with alkaline potassium ferricyanide has been described by G. Barger, F. Bergel, and A. R. Todd[13] and with porphyrexide by R. Kuhn and H. Vetter.[14] For thiochrome the former propose the structure (IV; $R = H$, $R_1 = C_2H_5$), whereas the latter authors favour a slightly different formula (IV; $R = R_1 = CH_3$).

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[3] *Ann. Reports*, 1934, **31**, 328.

[4] E. R. Buchman, R. R. Williams, and J. C. Keresztesy, *J. Amer. Chem. Soc.*, 1935, **57**, 1849.

[5] H. T. Clarke and S. Gurin, *ibid.*, p. 1876.

[6] M. Tomlinson, *J.*, 1935, 1030.

[7] R. R. Williams, E. R. Buchman, and A. E. Ruehle, *J. Amer. Chem. Soc.*, 1935, **57**, 1093; *A.*, 1035.

[8] T. W. Birch and L. J. Harris, *Nature*, 1935, **135**, 654.

[9] R. C. G. Moggridge and A. G. Ogston, *Biochem. J.*, 1935, **29**, 866; *A.*, 668.

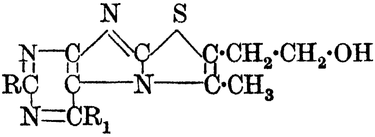
[10] *J. Amer. Chem. Soc.*, 1935, **57**, 1856.

[11] *Nature*, 1935, **135**, 107; *A.*, 415.

[12] *Z. physiol. Chem.*, 1935, **234**, 196; *A.*, 1026.

* The formula as originally published (and in the *Abstract*) gave the HCl attached to the S of the thiazole ring. This was undoubtedly a misprint.

(IV.)



Oxidation of vitamin B_1 with barium permanganate has been studied by A. Windaus, R. Tschesche, and R. Grewe,[15] who have isolated in small quantities some as yet unidentified pyrimidine derivatives.

The vitamin formula (III) appears to be in agreement with the properties of the substance, although some doubt exists as to whether the pyrimidine part carries one ethyl group in position 4, or two methyl groups in positions 2 : 4. Evidence from *C*-alkyl determinations in favour of the former view is advanced by A. R. Todd, F. Bergel, and Karimullah.[16] Final decision must, however, rest with synthesis.

Indeed, since the complete identification by analytical methods of the pyrimidine obtained by Williams is evidently very difficult, it seems likely that further advances in our knowledge of the structure of vitamin B_1 will be made mainly by synthesis. There seems little doubt, however, that the formula proposed by Williams is essentially correct.

The antineuritic activity of crystalline vitamin B_1 towards human beri-beri has been confirmed by R. R. Williams, R. E. Waterman, and J. C. Keresztesy,[17] who report also that the crystals completely protect rats from polyneuritis in a dose of 1—2 × 10^{-6} g. per day. A. J. Hermano and F. Eubanan[18] report the successful treatment of a number of cases of human beri-beri with crystalline aneurin.

Vitamin B_2.—The chemistry of the flavins is fully reviewed elsewhere in this volume.[19] It is sufficient here to mention that, although the synthetic arabinose derivative of alloxazine mentioned in the Report for last year [20] is undoubtedly physiologically active, it now appears that 6 : 7-dimethyl-9-*d*-riboflavin is chemically and physiologically identical with lactoflavin from milk.[21] The amyl derivative prepared last year,[22] and a similar substance with an acetic acid [23] side chain, are inactive.

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[13] *Nature*, 1935, **136**, 259; *A.*, 1286; *Ber.*, 1935, **68**, [*B*], 2257.

[14] *Ber.*, 1935, **68**, [*B*], 2375.

[15] *Z. physiol. Chem.*, 1935, **237**, 98.

[16] *Ber.*, 1936, **69**, [*B*], 217.

[17] *Science*, 1935, **81**, 535; *A.*, 1035.

[18] *Philippine J. Sci.*, 1935, **57**, 277; *A.*, 1429.

[19] **P. 354.**

It has been shown by H. Theorell [24] that no yellow enzyme is formed when lactoflavin is added to the inactive (protein) constituent of the enzyme, but that the prosthetic group is a monophosphoric ester of a flavin. Such a substance has been synthesised by R. Kuhn and H. Rudy,[25] who found it to behave similarly to the active group of the yellow enzyme in an electric field, but to be less active in causing decolorisation of methylene-blue.

P. György [27] has confirmed his previous finding [26] of the inactivity of lactoflavin in preventing "rat pellagra," for which another substance, which he terms B_6, is necessary. This substance is present in Peters' "charcoal eluate" from yeast, and György suggests that it may be a second natural pigment. In foodstuffs its concentration by no means parallels that of lactoflavin. These results are confirmed by L. J. Harris [28] and by H. Chick, A. M. Copping, and C. E. Edgar.[29] György recommends that the term "B_2" be applied to the lactoflavin plus B_6.

Vitamin C.—A large number of papers have dealt with the oxidative methods of determining *l*-ascorbic acid and with the various means available for overcoming its tendency to oxidise spontaneously and for removing the interfering substances (*e.g.*, glutathione) with which it is frequently associated.

B. C. Guha and A. R. Ghosh [30, 31, 32] report that rat tissues, especially liver, spleen, and kidney, are able to synthesise ascorbic acid *in vitro* from mannose, but not from glucose, fructose, galactose, xylose, or arabinose. Rats are known to be independent of vitamin C from external sources, unlike, *e.g.*, the ox, cat,[32] and guinea pig,[31] whose tissues are unable to synthesise the vitamin *in vitro*.

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[20] *Ann. Reports*, 1934, **31**, 329.

[21] H. von Euler, P. Karrer, M. Malmberg, K. Schöpp, F. Benz, B. Becker, and P. Frei, *Helv. Chim. Acta*, 1935, **18**, 522; *A.*, 760; R. Kuhn, K. Reinemund, F. Weygand, and R. Ströbele, *Ber.*, 1935, **68**, [*B*], 1765; *A.*, 1382.

[22] R. Kuhn and F. Weygand, *ibid.*, 1934, **67**, [*B*], 2084; *A.*, 262.

[23] R. Kuhn and H. Rudy, *ibid.*, 1935, **68**, [*B*], 300; *A.*, 503.

[24] *Biochem. Z.*, 1934, **275**, 37; *A.*, 248; *ibid.*, 1935, **275**, 344; *A.*, 400; *ibid.*, 1935, **278**, 263; *A.*, 1024.

[25] *Ber.*, 1935, **68**, [*B*], 383; *A.*, 545.

[26] *Ann. Reports*, 1934, **31**, 331.

[27] *Biochem. J.*, 1935, **29**, 741, 760, 767; *A.*, 545.

[28] *Ibid.*, p. 776; *A.*, 545.

[29] *Ibid.*, p. 722; *A.*, 544.

[30] *Nature*, 1934, **134**, 739; *A.*, 1934, 131.

[31] *Current Sci.*, 1934, **3**, 251; *A.*, 1934, 416.

[32] *Nature*, 1935, **135**, 871; *A.*, 903.

Vitamin D.—It is well established that a particular physiological activity is frequently possessed by a group of related substances, although one (or a few) of the group may possess it in an outstanding degree. Among the hormones and vitamins this phenomenon appears to exist to an extent which was unsuspected a year or two ago. The fact that oestrogenic activity is possessed by a number of substances other than oestrone and oestriol has been known for some time, and has been commented on in these Reports ;[33] it was noted last year also that certain modifications in the structure of the testicular hormone and that of the corpus luteum resulted in increased rather than decreased activity. During the past year several other substances, hormones and vitamins, have been shown not to be alone in possessing their peculiar activities, and in one case, that of vitamin D, the question has been raised as to whether the substance hitherto regarded as the vitamin is really entitled to be so considered.

W. C. Russell, M. W. Taylor, and D. E. Wilcox [34] found that, with chickens, in order to induce normal growth and produce bone of normal composition it was necessary to supply at least 144 times as much vitamin D in the form of irradiated ergosterol as in the form of cod-liver oil. Irradiated ergosterol was also less efficacious than cod-liver oil in maintaining laying in pullets. M. J. L. Dols [35] found that, whereas chickens were adequately protected from rickets by a diet containing 2% of cod-liver oil, the addition of irradiated ergosterol with a vitamin activity (as measured on rats) ten times as great was insufficient. Two hundred and fifty international (rat) units of vitamin D per 100 g. of ration sufficed for chicks when supplied in the form of cod-liver oil, unsaponifiable fraction of cod-liver oil, tunny oil concentrate, or irradiated cholesterol, but 2500 units as irradiated ergosterol were insufficient. The obvious conclusion is that the antirachitic substance in the fish oils is not identical with calciferol. Similar results have been obtained before, though perhaps in less conclusive form. It has, of course, to be remembered that other substances present in the fish oils, *e.g.*, vitamin A, may be exerting some effect. Indeed, T. G. H. Drake, F. F. Tisdall, and A. Brown [36] have found the opposite effect in infants—that irradiated ergosterol has a greater antirachitic effect than an equal number of rat units of vitamin D in the form of cod-liver oil. The same criticism has been levelled against the work of F. Ender,[37] who reported chemical and physical differences between a vitamin D concentrate from natural sources and the substance obtained by irradiating ergosterol. O. Rygh [38] has now reported that vitamin D concentrates from the liver fats of a woman, a cow, and numerous species of fish were equally effective in preventing rickets in chicks and agreed further in showing no absorption maximum at 260—270 mμ, no rotation in alcoholic solution, no reaction with maleic anhydride, and complete esterification in 10 days with phthalic anhydride and pyridine. These findings indicate quite definitely that antirachitic activity is not confined to calciferol, and strongly suggest, indeed, that calciferol is not the natural vitamin. The latter conclusion, however, must still be regarded with some reserve, in view of the wide distribution of ergosterol. The nature of the antirachitic substance in the liver-oil concentrates of Rygh is still unknown.

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[33] *Ann. Reports*, 1934, **31**, 326.

[34] *J. Biol. Chem.*, 1934, **107**, 735; *A.*, 1935, 261.

[35] *Diss.*, Nijmegen, 1935; *A.*, 1430.

[36] *Canadian Med. Assoc. J.*, 1934, **71**, 368; *A.*, 1935, 417.

In addition to calciferol and a naturally occurring substance not identical with it, other, artificially prepared, substances are now known to be antirachitic. A reduction product of ergosterol (22 : 23-dihydroergosterol) becomes strongly antirachitic when heated, and further evidence that the side chain is of relatively little importance in determining activity is afforded by the fact that irradiation of 7 : 8-dehydrocholesterol (side chain of 8 instead of 9 C) gives a product containing 8000 antirachitic units per mg.[39] Dehydrocholesterol has the same spectrum as ergosterol, and is strongly lævorotatory; it would therefore appear not to be the precursor of the substance which Rygh believes to be the natural vitamin.

The constitution of calciferol is not yet completely determined, although the different workers agree that it contains a three-ring system, ring scission taking place during irradiation in the conversion of lumisterol into tachysterol, and the four-ring system being re-formed when calciferol is converted into pyrocalciferol. O. Rosenheim and H. King [40] favour a formula (V) having a 10-membered ring, with three conjugated double bonds, of which one is in the original ring C of the sterol system.

I. M. Heilbron, K. M. Samant, and F. S. Spring [41] also suggest a three-ring formula. I. M. Heilbron and F. S. Spring[42] agree with Rosenheim and King that the change from tachysterol to calciferol involves a change in the position of the double bonds, but do not think the position of these bonds can yet be decided with certainty.

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[37] *Z. Vitaminforsch.*, 1933, **2**, 241.

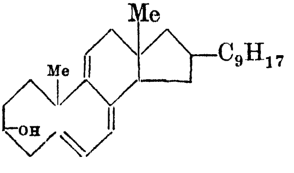
[38] *Nature*, 1935, **136**, 396, 662; *A.*, 1430.

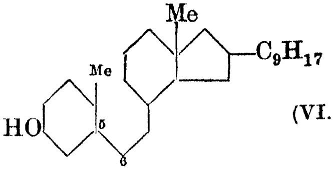
[39] A. Windaus, H. Lettré, and F. Schenck, *Annalen*, 1935, **520**, 98; *A.*, 1363.

[40] *Chem. and Ind.*, 1935, 699; *A.*, 1120.

[41] *Nature*, 1935, **135**, 1072; *A.*, 1036.

(V.)





(VI.)

From consideration of the effects of mild oxidation on calciferol they hold that the ring system shown in (VI) must be present in calciferol, and that one of the double bonds occupies the 5 : 6-position.

Windaus[43] suggests a similar ring scission.

Vitamin E.—Although vitamin E has not yet been isolated, increased knowledge of its chemical character should lead before long to its preparation in a pure state. It is known to be an alcohol.[44] Benzoyl and acetyl derivatives of concentrates from vitamin-E-active oils show the vitamin activity, but methyl or ethyl ethers, and also a urethane obtained by the action of phenyl *iso*cyanate, do not. Alcoholic potassium hydroxide, however, hydrolyses the urethane and restores activity. The vitamin concentrates exhibit an absorption band at 294 mμ, but H. S. Olcott[45] concludes that this is not due to the vitamin, since its intensity is not proportional to the vitamin activity. Hydrogenation of the active concentrates reduces the iodine value to 26 and does not destroy the active substance.

J. C. Drummond, E. Singer, and R. J. Macwalter[46] have obtained a concentrate, active in a daily dose of 0·1 mg., and evidently containing a hydroxyl group, since it is capable of acetylation. They describe their preparations, however, as showing an absorption band at 294 mμ, the intensity of which is proportional to the vitamin activity of the preparation. They found that acetylation of their active product yielded β-amyrin acetate, which was inactive and gave little absorption. This is, however, not the vitamin, since Olcott found that his acetylated product was active, and F. E. Askew[47] from examination of surface films has concluded that β-amyrin differs from vitamin E, which, however, may be a polycyclic compound with a water-attracting group near one end of the molecule.

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[42] *Chem. and Ind.*, 1935, 795; *A.*, 1235.

[43] Cf. H. Müller, *Z. physiol. Chem.*, 1935, **233**, 223; *A.*, 1037.

[44] H. S. Olcott, *J. Biol. Chem.*, 1935, **110**, 695; *A.*, 1287.

[45] *Ibid.*, 1934, **107**, 471; *A.*, 1935, 129.

[46] *Biochem. J.*, 1935, **29**, 456; *A.*, 418.

[47] *Ibid.*, p. 472; *A.*, 418.

The Sex Hormones.

The number of publications dealing with the sex hormones has suffered no diminution. The interest still lies mainly in the chemical constitution of the hormones and its relation to physiological activity.

Testicular Hormone.—It was reported last year[48] that androsterone, prepared from urine and from *epi*dihydrocholesterol, appeared to be somewhat specific, although its reduction product, androstanediol, was even more active in promoting comb growth in the capon. During the year under review the number of active substances has been considerably increased, both by isolation from natural sources and by artificial preparation.

Androsterone (VII) is saturated, and has the spatial arrangement shown; its stereoisomeride, *iso*androsterone (VIII),[49] obtainable from dihydrocholesterol or stigmasterol, is about one-tenth as active in the comb-growth test;[50] but the corresponding compounds with the *cis*-arrangement of rings A and B are inactive. The particular stereo-position of the hydroxyl group in androsterone does not, therefore, appear to be essential for physiological activity, and, indeed, androstanedione[50, 52] (IX) (isolated from testes[51]) is about two-thirds as active as androsterone in promoting comb growth (*in vivo* reduction may occur, of course). A point of some importance arises here, for when tested by its power of stimulating vesicular growth in immature or castrated rats, androstanedione is found to be somewhat more active than androsterone; on the other hand, androstanediol (X) is four or five times as active as androsterone in promoting comb growth,[53] but only slightly more active in promoting vesicular growth.[54]

It seems, further, that, although compounds with the *cis*-arrangement of rings A and B are inactive, the presence of a *trans*-arrangement is not essential, for several active unsaturated substances have been discovered. Butenandt [55] isolated from urine *iso*dehydroandrosterone (XI), which was about as active as *iso*androsterone [56]

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[48] *Ann. Reports*, 1934, **31**, 323.

[49] A. Butenandt and H. Cobler, *Z. physiol. Chem.*, 1935, **234**, 218; *A.*, 1033.

[50] L. Ruzicka and A. Wettstein, *Helv. Chim. Acta*, 1935, **18**, 986; *A.*, 1125.

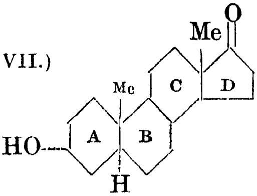
[51] A. Ogata and S. Hirano, *J. Pharm. Soc. Japan*, 1934, **54**, 199.

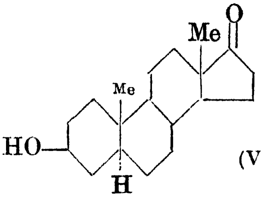
[52] A. Butenandt and K. Tschernig, *Z. physiol. Chem.*, 1934, **229**, 185; *A.*, 1935, 413.

[53] L. Ruzicka, M. W. Goldberg, and J. Meyer, *Helv. Chim. Acta*, 1935, **18**, 210; *A.*, 346; A. Butenandt and K. Tschernig, *Z. physiol. Chem.*, 1935, **234**, 224; *A.*, 1033.

[54] E. Tschopp, *Nature*, 1935, **136**, 259; *A.*, 1285.

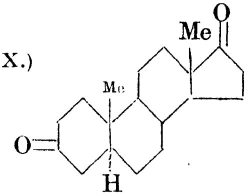
(VII.)

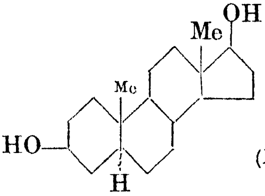




(VIII.)

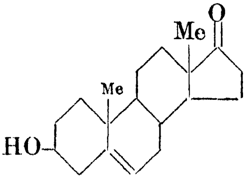
(IX.)



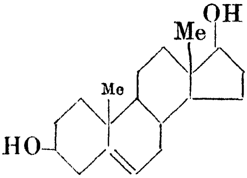


(X.)

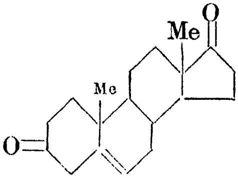
and was shown by its preparation from cholesterol to have the structure (XI).[50, 57] On reduction it gave the only slightly active dihydroxy-compound (XII),[58] but oxidation produced androstenedione [59] (XIII), which is less active than androsterone in the comb-growth test (about two-thirds) and about twice as active in the rat test.



(XI.)



(XII.)



(XIII.)

Most active of all is testosterone (XIV), isolated from testes by Laqueur *et al.*,[60] and shown by Butenandt [58, 61] and by Ruzicka,[62] who prepared it from *iso*dehydroandrosterone, to have the structure shown, which is remarkably similar to that of progesterone (XV). It is about five times as active as androsterone in the comb-growth test and about twenty times as active in promoting vesicular growth.

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[55] A. Butenandt and H. Dannenbaum, *Z. physiol. Chem.*, 1934, **229**, 192; *A.*, 1935, 413.

[56] *Idem*, and G. Harrisch and H. Kudszus, *ibid.*, 1935, **237**, 52.

[57] E. S. Wallis and E. Fernholz, *J. Amer. Chem. Soc.*, 1935, **57**, 1379, 1504, 1511; *A.*, 1125, 1242.

[58] A. Butenandt and G. Hanisch, *Z. physiol. Chem.*, 1935, **237**, 89.

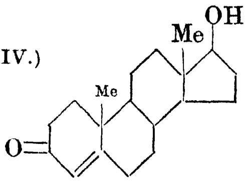
[59] A. Butenandt and H. Kudszus, *ibid.*, p. 75.

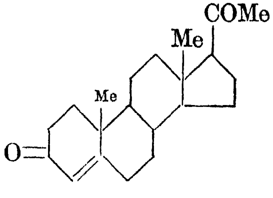
[60] K. David, E. Dingemanse, J. Freud, and E. Laqueur, *ibid.*, 1935, **233**, 281; *A.*, 1033.

[61] A. Butenandt and G. Hanisch, *Ber.*, 1935, **68**, [*B*], 1859; *A.*, 1370.

[62] L. Ruzicka and A. Wettstein, *Helv. Chim. Acta*, 1935, **18**, 1264; *A.*, 1371.

(XIV.)





(XV.)

The figures representing relative activities cannot be given more than approximately, for, as in all biological tests, there is a considerable margin of error, and such conditions as time elapsing since castration, duration of test, age and breed of animal, size of dose (*i.e.*, whether an average or a maximal effect is sought) all affect the results of the test.[54, 63] There seems no doubt, however, that testosterone is the most active substance yet obtained in this group, and the tendency is to regard it as the true hormone, and to consider androsterone and the other naturally occurring related substances as products of its metabolism.

The Corpus Luteum Hormone.—It has been suggested that the names α- and β-progesterone be used for the high- and the low-melting form, respectively, of the corpus luteum hormone, previously known as progestin or luteosterone.[64] The two forms, it is now agreed, are chemically and biologically identical: W. M. Allen and S. R. M. Reynolds [65] have shown that both suppress uterine mobility in rabbits, and that both inhibition of motility and progestational proliferation of the endometrium are produced by one and the same hormone. Progesterone still seems to be remarkably specific. Reduction of both keto-groups or of the C_{20} keto-group yields inactive compounds,[66] and a second hydroxy-ketone, *allo*-pregnan-3-ol-20-one, isolated from corpus luteum is also inactive.[67] Not only is activity dependent on the presence of both ketone groups, but the presence and the position of the double bond are both important. Pregnandione, the saturated diketone corresponding to progesterone, is inactive and has been converted by

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[63] L. Ruzicka, M. W. Goldberg, and H. R. Rosenberg, *Helv. Chim. Acta*, 1935, **18**, 1487.

[64] W. M. Allen, A. Butenandt, G. W. Corner, and K. H. Slotta, *Z. physiol. Chem.*, 1935, **235**, 1; *Nature*, 1935, **136**, 303; *A.*, 1284.

[65] *Science*, 1935, **82**, 155.

[66] *Ann. Reports*, 1934, **31**, 327.

[67] A. Butenandt and L. Mamoli, *Ber.*, 1934, **67**, [*B*], 1897; *A.*, 1935, 215; E. Fernholz, *Z. physiol. Chem.*, 1934, **230**, 185; *A.*, 1935, 215.

A. Butenandt and L. Mamoli [68] into a singly unsaturated diketone (believed to be Δ^1-*allo*pregnene-3 : 20-dione) which is devoid of activity.

Chemistry of Muscle.

Reference was made last year [69] to attempts to co-ordinate the various chemical changes known to be associated with muscular activity. Much important work has been published during 1935 on the details of lactic acid formation; it is, however, in the continuation of the attempts at co-ordination that the main interest of the year's work lies. The position at present is by no means clear, for the problem of muscle chemistry involves the problem of the chemistry of muscular contraction, and of this, glycogenolysis forms only a part. The main progress so far is in the co-ordination of the changes in the phosphorus-containing compounds with lactic acid formation and, generally speaking, in the clear recognition of the key position occupied by these substances and of glycogenolysis as a series of reactions involving the transference of phosphate from one molecule to another.

Adenylic acid pyrophosphate is apparently required for the formation of phosphoric esters of carbohydrate (acting as phosphoric acid donator), but the only other stage in lactic acid formation at which co-enzyme is necessary appears to be the hydrolysis of phosphopyruvic acid. At this stage it is now evident that adenylic acid is probably the true co-enzyme (acting as phosphoric acid acceptor).

P. Ostern *et al.*[70] have shown that autolysed frog-muscle extract slowly hydrolyses phosphoglyceric acid, but if adenylic acid is added, adenylic acid pyrophosphate is slowly formed and, with phosphopyruvic acid, accounts for all the phosphorus. In absence of creatine, phosphoglyceric acid is converted in part into phosphopyruvic acid and no PO_4''' is liberated; in this case adenylic acid then causes rapid production of adenylic acid pyrophosphate to an extent which accounts for half the phosphorus of the phosphoglyceric acid. It is therefore concluded that the "dephosphorylation" of phosphoglyceric acid takes place in two stages and that (contrary to the earlier hypothesis of J. K. Parnas, P. Ostern, and T. Mann [69]) creatine-phosphoric acid is not an obligatory intermediary.

[It is probable, from studies with natural and with synthetic phosphopyruvic acid,[71, 72, 73, 74] $CH_2\text{:}C(O{\cdot}PO_3H){\cdot}CO_2H$, that 3-phosphoglyceric acid (formed from triose phosphoric acid) is converted by the action of a "phosphoglyceromutase" into 2-phosphoglyceric acid; that this, under the influence of "enolase," yields phosphopyruvic acid; and that phosphoric acid is then transferred to adenylic acid (or creatine) with liberation of pyruvic acid.]

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[68] *Ber.*, 1935, **68**, [*B*], 1850; *A.*, 1370.

[69] *Ann. Reports*, 1934, **31**, 338.

[70] P. Ostern, T. Baranowski, and J. Reis, *Compt. rend. Soc. Biol.*, 1935, **118**, 1414; *A.*, 778.

Similar results have been published still more recently by P. Ostern, T. Baranowski, and J. Reis,[75] who find that dephosphorylation of phosphoglyceric acid can occur only in presence of adenylic acid or adenylic acid pyrophosphate : if creatine also is present, formation of phosphocreatine occurs only under conditions which lead to an accumulation of adenylic acid pyrophosphate from adenylic acid. Under certain conditions in the system, phosphoglyceric acid–adenylic acid–creatine–phosphocreatine, there may be transference of phosphate from molecule to molecule (with liberation of pyruvic acid) without the liberation of any PO_4'''.

D. M. Needham and W. E. van Heyningen [76] also have found that phosphoglyceric acid is converted into pyruvic acid by dialysed muscle preparations in the presence of adenylic acid or adenylic acid pyrophosphate, though not in the presence of creatine without adenylic compounds. When adenylic acid was present, even without creatine, adenylic acid pyrophosphate was formed in amount equivalent to the whole of the adenylic acid present; when creatine was present with adenylic acid, phosphocreatine was formed as well. By using extracts dialysed for a long time so as to destroy the enzyme responsible for the hydrolysis of adenylic acid pyrophosphate to adenylic acid and phosphoric acid, Needham and van Heyningen were able to show that in all probability adenylic acid pyrophosphate itself is incapable of inducing dephosphorylation of phosphoglyceric (or phosphopyruvic) acid, and that adenylic acid is the real co-enzyme in this reaction. This conclusion, though contradicting the earlier statement of K. Lohmann and O. Meyerhof,[77] is in agreement with the views recently published by O. Meyerhof and Lehmann.[78] Adenylic acid pyrophosphate can, usually, function as a co-enzyme on account of its rapid hydrolysis to adenylic acid.

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[71] W. Kiessling, *Ber.*, 1935, **68**, [*B*], 243; *A.*, 471.

[72] *Idem, ibid.*, p. 597; *A.*, 731.

[73] O. Meyerhof and W. Kiessling, *Biochem. Z.*, 1935, **280**, 99; *A.*, 1418.

[74] R. Akano, *ibid.*, p. 110.

[75] *Ibid.*, 1935, **279**, 85; *A.*, 1150.

[76] *Biochem. J.*, 1935, **29**, 2040; *A.*, 1278.

[77] *Biochem. Z.*, 1934, **271**, 264.

[78] *Naturwiss.*, 1933, **21**, 337.

Since the reaction, phosphoglyceric acid + creatine = pyruvic acid + phosphocreatine + H_2O, is now shown not to take place, and since J. K. Parnas *et al.*[79] have demonstrated an increase in phosphocreatine when frog-muscle pulp poisoned with iodoacetate is incubated with phosphoglyceric acid (confirmed by the authors cited above), Needham and van Heyningen and also J. K. Parnas and P. Ostern[80] make the suggestion, which is in agreement with the results of Ostern *et al.*[70] as well as their own, that phosphocreatine may be synthesised by a reverse Lohmann reaction, *i.e.*,

adenylic acid pyrophosphate + creatine = phosphocreatine + adenylic acid.

Needham and van Heyningen suggest further that, since this is a termolecular reaction, it may proceed in two stages, with intermediate formation of adenosine diphosphate, which has been found by K. Lohmann[81] in heart and smooth muscle and whose reaction with phosphoarginine has been demonstrated in crab muscle. This suggestion is an interesting one, for it is to be supposed that the (in skeletal muscle) exceedingly labile adenosine diphosphate would occur transitorily as an intermediate in the formation of adenosine triphosphate (adenylic acid pyrophosphate) from adenylic acid. It would thus account for the finding, recorded above, that phosphocreatine synthesis occurs in circumstances which lead to accumulation of adenylic acid pyrophosphate and also for the fact that ordinarily, in resting muscle, the amount of phosphocreatine slowly decreases.

The present position is, therefore, that glycogenolysis does not necessarily involve the intervention of phosphocreatine, but consists essentially in (1) the transference of phosphate from adenylic acid pyrophosphate to carbohydrate; (2) the production of glycerophosphoric acid and phosphopyruvic acid from the hexose diphosphoric acid so formed; (3) the dephosphorylation of phosphopyruvic acid, the phosphate being transferred to the adenylic acid formed in (1); (4) the reduction of pyruvic acid to lactic acid with simultaneous oxidation of glycerophosphoric acid.

In addition to the co-enzymes adenylic acid and adenylic acid pyrophosphate, which take part in certain reactions in stoicheiometric proportions, the glycogenolysis system also requires magnesium ions. Their function is still obscure. Nor is it known how inorganic phosphate may enter or leave the system (as it does *in vitro* at least).

The relation of phosphocreatine to these reactions is by no means clear. It is, apparently, not hydrolysed by a specific enzyme, but liberates creatine by transferring its phosphate to adenylic acid.[69] On the other hand, it can, in certain circumstances, be resynthesised at the expense of adenylic acid pyrophosphate (or possibly adenosine diphosphate). It has, therefore, been described as a reserve of phosphate, a phosphate donator for the rapid resynthesis of adenylic acid pyrophosphate.[80] This, however, leaves unexplained many facts of muscle chemistry, and a further clarification of the position is required.

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[79] J. K. Parnas, P. Ostern, and T. Mann, *Biochem. Z.*, 1934, **275**, 74; *A.*, 1935, 239.

[80] *Ibid.*, 1935, **279**, 94; *A.*, 1150.

[81] *Angew. Chem.*, 1935, **48**, 165.

The question of ammonia production has received attention from J. K. Parnas and his collaborators. They are of the opinion that adenylic acid, but not adenylic acid pyrophosphate, may undergo deamination,[82] but experiments (*e.g.*, on the inhibition by phosphoglyceric acid of ammonia production in muscle pulp poisoned by fluoride or iodoacetic acid [83, 84]) lead them to believe that this deamination takes place when glycogenolysis is completed, *i.e.*, that adenylic acid is preferentially rephosphorylated to adenylic acid pyrophosphate. During the resting stage re-amination of inosinic acid is possible.[82]

Fat Metabolism.

It has long been held, as suggested by Knoop, that oxidation of fatty acids *in vivo* takes place by successive oxidations of the β-carbon atom, and, though it has been questioned whether this is the sole mode of oxidation, β-oxidation has been generally accepted as accounting for the main part of fatty acid oxidation. Recently, definite proof has been advanced that other processes of oxidation occur, and even the general theory of β-oxidation, at least in its usual form, has been called into question.

P. E. Verkade and J. van der Lee [85] found that, after the feeding (to man) of triglycerides of fatty acids containing from 8 to 12 carbon atoms, the corresponding dicarboxylic acids were excreted in the urine. There was no difference between the fatty acids, attributable to their possession of an odd or an even number of carbon atoms, but the formation of dicarboxylic acid was greatest in the case of tricaprin. When tricaprin was fed, the urine contained not only sebacic acid, but also small amounts of the lower dicarboxylic acids, adipic and suberic. These results Verkade and van der Lee explained as due to combined ω- and β-oxidation, the possible routes being:

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[82] J. K. Parnas, P. Ostern, and T. Mann, *Rocz. Chem.*, 1934, **14**, 1358; *A.*, 1935, 387.

[83] T. Mann, *Biochem. Z.*, 1935, **277**, 380; *A.*, 890.

[84] *Idem, ibid.*, 1935, **279**, 82; *A.*, 1150.

[85] *Biochem. J.*, 1934, **28**, 31; *A.*, 1934, 441; *Z. physiol. Chem.*, 1934, **227**, 213; *A.*, 1934, 1393.

$$\begin{tikzcd}
CH_3\cdot[CH_2]_8\cdot CO_2H \arrow[r, "\omega"] \arrow[d, "\beta"] & HO_2C\cdot[CH_2]_8\cdot CO_2H \arrow[d, "\beta"] \\
CH_3\cdot[CH_2]_6\cdot CO_2H \arrow[r, "\omega"] \arrow[d, "\beta"] & HO_2C\cdot[CH_2]_6\cdot CO_2H \arrow[d, "\beta"] \\
CH_3\cdot[CH_2]_4\cdot CO_2H \arrow[r, "\omega"] & HO_2C\cdot[CH_2]_4\cdot CO_2H
\end{tikzcd}$$

The existence of ω-oxidation has been confirmed by B. Flaschenträger, K. Bernhard, C. Löwenberg, and M. Schläpfer,[86] who, after feeding α-methylbenzosulphaminolauric acid (to dogs), isolated the similarly substituted adipic acid from the urine. The authors postulate an initial ω-oxidation, followed by three successive β-oxidations. B. Flaschenträger and K. Bernhard [87] have also obtained sebacic acid from dog's urine after feeding sodium decoate and sodium laurate (0·5—1·0% of the fatty acid fed) and in the case of sodium decoate they obtained suberic acid as well. Similar results were obtained with methyl decoate and with ethyl (but not methyl) laurate.

P. E. Verkade and J. van der Lee [88] also have obtained evidence of direct oxidation, with rupture of the chain, at the double bond of an unsaturated acid, for they found that after ingestion of tri-Δ^{ι}-undecenoin, sebacic acid was excreted in the urine. They were unable, however, to isolate any definite acids after the ingestion of olive or rape oil.

M. Jowett and J. H. Quastel [89] have studied the oxidation of fatty acids by liver slices. They first investigated the production of acetoacetic acid from butyric, crotonic, and β-hydroxybutyric acids, and from mixtures of these. From (*inter alia*) the fact that crotonic and butyric acids appeared to compete for oxidation, whereas hydroxybutyric acid showed a partial additive effect, they concluded that hydroxybutyric acid was not an intermediary in acetoacetic acid formation. Since, moreover, acetoacetic acid was produced more rapidly from butyric than from crotonic acid, since certain inhibitors affected oxidation of crotonic acid more than that of butyric acid, and since the optimal rate of oxidation required a higher concentration of crotonic than of butyric acid, they decided against desaturation with formation of crotonic acid as the first stage in the oxidation of butyric acid. They suggest an activation of butyric acid to a product identical with activated crotonic acid :

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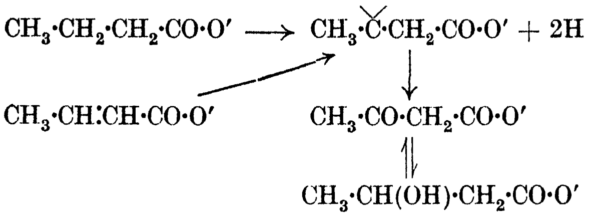
[86] *Z. physiol. Chem.*, 1934, **225**, 157; *A.*, 1934, 1027.

[87] *Naturwiss.*, 1935, **23**, 356; *A.*, 1015; *Helv. Chim. Acta*, 1935, **18**, 962; *A.*, 1151.

[88] *Z. physiol. Chem.*, 1934, **230**, 207; *A.*, 1935, 242; *Proc. K. Akad. Wetensch. Amsterdam*, 1934, **37**, 590; *A.*, 1935, 390.

[89] *Biochem. J.*, 1935, **29**, 2143; *A.*, 1408.



$$\begin{tikzcd}
CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O' \arrow[r] & CH_3{\cdot}\overset{\vee}{C}{\cdot}CH_2{\cdot}CO{\cdot}O' + 2H \arrow[d] \\
CH_3{\cdot}CH{:}CH{\cdot}CO{\cdot}O' \arrow[ur] & CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}O' \arrow[d, shift left] \\
 & CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}O' \arrow[u, shift left]
\end{tikzcd}$$

According to this view, then, oxidation of the fatty acid chain consists in production of a keto-acid by addition of oxygen after desaturation to an activated ion which exists only in association with the enzyme.

Jowett and Quastel[90] have further investigated the oxidation, by liver slices, of normal saturated fatty acids containing from 2 to 10 carbon atoms. They find that, with guinea-pig liver, all except propionic acid yield acetoacetic acid, which is probably the only keto-acid produced in significant amount. The acids containing an odd number of carbon atoms produce only small amounts of acetoacetic acid; hexoic and octoic acids produce about one mol. of ketonic compounds per mol. of acid; decoic acid produces rather less, butyric acid considerably less, and acetic acid even less than the higher odd-numbered fatty acids. The fatty acids higher than valeric, especially those with an even number of carbon atoms, produce some " fixed " acid, which is not acetoacetic or hydroxybutyric acid but has not been positively identified; with acetic, valeric, and propionic acids, however, there is a disappearance of " fixed " acid, and with butyric there is a very slight loss. With rat liver, sodium benzoate inhibits acetoacetic acid production from the even-numbered fatty acids, the inhibition being greatest with butyric acid and decreasing as the series is ascended. N. L. Edson[91] also has found that in liver slices odd-numbered fatty acids give rise to β-ketonic acid (acetoacetic acid, according to Jowett and Quastel), though only to about one-third the extent of the even-numbered acids, and this fact alone is clearly incompatible with the idea of successive β-oxidations as the only mode of breakdown of fatty acids. J. S. Butts *et al.*[92] support this conclusion with experiments on the intact rat, suggesting that octoic acid may be oxidised to two molecules of ketonic compounds. Jowett and Quastel point out that the difficulty cannot be overcome by supposing the production, by β-oxidation, of acetic acid, which might then be transformed into acetoacetic acid, since their quantitative results are against such a supposition. Taking into account any possible formation of acetoacetic acid from acetic acid, they consider the lower formation of acetoacetic acid by butyric than by hexoic, octoic, and decoic acids, together with the differing inhibiting effect of sodium benzoate, to be fatal to the β-oxidation theory. To replace it, they suggest a hypothesis of "multiple alternate oxidation," according to which the fatty acids undergo an oxidation throughout the chain, alternate carbon atoms being affected. Thus octoic acid may be supposed to be oxidised at the β-, δ-, and ζ-carbon atoms simultaneously (possibly at the α-, γ-, and ε-carbon atoms to some extent), and valeric acid might undergo either β-oxidation or oxidation at the α- and γ-carbon atoms. Oxidation at the β-, δ- . . . atoms is to be considered the main process in the oxidation of the higher fatty acids.

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[90] *Biochem. J.*, 1935, **29**, 2159; *A.*, 1408.

[91] *Ibid.*, p. 2082; *A.*, 1273.

[92] J. S. Butts, C. H. Cutler, L. Hallman, and H. J. Deuel, jun., *J. Biol. Chem.*, 1935, **109**, 597; *A.*, 891.

The liver slice technique has been applied by C. L. Gemmill and E. G. Holmes[93] to the vexed question of the conversion of fat into carbohydrate. They find that slices of liver from rats fed on butter have an R.Q. of 0·58 (0·79 for slices from rats on normal diet), and that, after being shaken for 3 hours in sodium bicarbonate–Ringer solution at 37°, the slices show an increased carbohydrate content. The glycogen content of the livers of rats fed on butter falls almost to zero on the first day of the diet, and then gradually increases to a maximum of 1% on the fourth or fifth day. Although the latter results could conceivably be explained by transference of glycogen from other tissues, those with liver slices afford strong evidence in favour of carbohydrate production from fat (though the possibility of formation from protein is not definitely eliminated).

Amino-acids.

Last year[94] the synthesis was reported of four diketopiperazines which underwent hydrolysis by digestive enzymes. Two of them, containing amino-dicarboxylic acids, were hydrolysed by trypsin and papain, and the others, containing diaminopropionic acid, were hydrolysed by pepsin. Y. Tazawa[95] has now obtained *d*-arginine anhydride tetrahydrochloride and *d*-lysine anhydride dihydrochloride. These substances are hydrolysed smoothly by pepsin, but not by trypsin or papain. It seems, therefore, that substituted

[93] *Biochem. J.*, 1935, **29**, 338; *A.*, 523.

[94] *Ann. Reports*, 1934, **31**, 342.

[95] *Acta Phytochim.*, 1935, **8**, 331; *A.*, 966.

diketopiperazines are susceptible to enzymic hydrolysis provided the side chains contain suitable amino- or carboxy-groups. This removes the main objection to accepting the diketopiperazine ring as part of the normal structure of proteins. Anhydrides have, of course, frequently been isolated from protein hydrolysates, though the methods employed have left open the possibility that they may be artefacts. Indirect evidence of their existence in the protein molecule is suggestive but inconclusive. The finding that they may be hydrolysed by digestive enzymes will surely stimulate the search for more conclusive evidence of their actual existence in the protein molecule.

New reagents and methods for determining the arrangement of the amino-acids within the protein molecule are being sought. S. Gurin and H. T. Clarke [96] have prepared the benzenesulphonyl derivative of gelatin and succeeded in hydrolysing the peptide linkages without splitting off the benzenesulphonyl group. From the yield of ε-benzenesulphonyl-*d*-lysine obtained, they conclude that at least 50% of the free NH_2 in gelatin is accounted for by the ε-NH_2 of lysine, and that not more than 0·5% can be due to mono-amino-acids. M. Bergmann [97] has used "rhodanilic acid," $[Cr(CNS)_4(C_6H_5{\cdot}NH_2)_2]H$, which gives a sparingly soluble crystalline salt with proline. On the basis of analysis of gelatin with this reagent, he suggests that every sixth amino-acid in the chain is proline, every ninth hydroxyproline, and every third glycine.

D. Blumenthal and H. T. Clarke [98] distinguish two types of sulphur compound, one oxidised to SO_4'' by bromine and giving lead sulphide on treatment with lead carbonate, the other oxidised to SO_4'' by fuming nitric acid and not affected by lead carbonate. Applying this result to protein hydrolysates, they find that, besides cystine and methionine, two other sulphur-containing substances are present, one of each type. A new sulphur-containing amino-acid is claimed to have been isolated by A. G. van Veen and A. S. Hyman,[99] who obtained it in 1·6% yield from the djenkol bean and named it djenkolic acid. It has the formula $CH_2[S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H]_2$ and on treatment with concentrated sulphuric acid gives cystine and simple decomposition products.

An interesting amino-acid is canavanine, which was isolated in 1929 by Kitagawa,[1] who considered it to be

$$NH_2{\cdot}C(:NH){\cdot}NH{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$$

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[96] *J. Biol. Chem.*, 1934, **107**, 395; *A.*, 1935, 101.

[97] *Ibid.*, 1935, **110**, 471; *A.*, 1140.

[98] *Ibid.*, p. 343; *A.*, 1140.

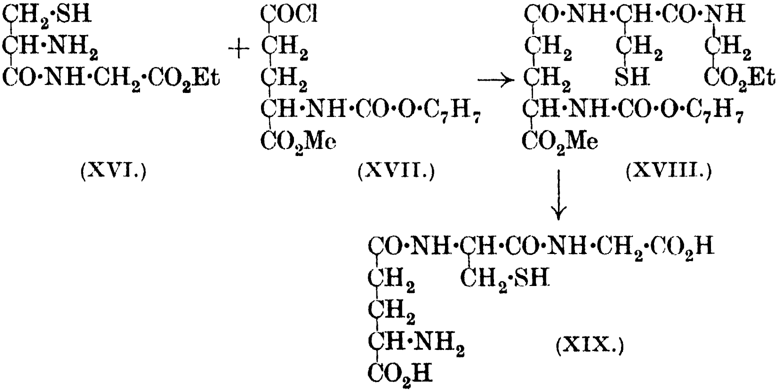
[99] *Rec. trav. chim.*, 1935, **54**, 493; *A.*, 966.

[1] M. Kitagawa and T. Tomita, *Proc. Imp. Acad. Tokyo*, 1929, **5**, 380; *A.*, 1930, 121.

and showed that it resembled arginine in being able to take part in the production of urea from ammonia and carbon dioxide. The constitution of canavanine has been confirmed by J. M. Gulland and C. J. O. R. Morris,[2] who found that chloramine-T converted it into a mixture of glyoxal and tartronic semialdehyde, and hot concentrated hydrobromic acid produced α-amino-γ-butyrolactone hydrobromide, ammonia, and guanidine.

Glutathione.

The tripiptide isolated by (Sir) F. G. Hopkins[3] in 1930 and almost simultaneously by E. C. Kendall, B. F. McKenzie, and H. L. Mason[4] has been shown by a number of workers to be γ-glutamylcysteylglycine. This constitution has now been confirmed by synthesis. The synthesis by C. R. Harington and T. H. Mead[5] is founded upon the benzylcarbonato-method of M. Bergmann and L. Zervas,[6] but its success is due to the discovery of a suitable means of removing the benzylcarbonato-residue, which was not achieved, in the case of cysteine-containing substances, by the original method of catalytic reduction. Reduction by phosphonium iodide in acetic acid was effective, however, and so overcame the main stumbling block in a very difficult synthesis. *N*-Carbobenzyloxycystine was converted into the acid chloride, which was coupled with glycine ester, and the product on reduction with phosphonium iodide yielded cysteylglycyl ester (XVI) (isolated as hydriodide). The α-monomethyl ester of *N*-carbobenzyloxyglutamic acid was obtained by the action of sodium methoxide in methyl alcohol on *N*-carbobenzyloxyglutamic



$$\begin{array}{l}CH_2{\cdot}SH\\ CH{\cdot}NH_2\\ CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et\end{array} + \begin{array}{l}COCl\\ CH_2\\ CH_2\\ CH{\cdot}NH{\cdot}CO{\cdot}O{\cdot}C_7H_7\\ CO_2Me\end{array} \longrightarrow \begin{array}{lll}CO{\cdot}NH{\cdot}CH{\cdot}CO{\cdot}NH & & \\ CH_2 \quad CH_2 & & CH_2\\ CH_2 \quad SH & & CO_2Et\\ CH{\cdot}NH{\cdot}CO{\cdot}O{\cdot}C_7H_7 & & \\ CO_2Me & & \end{array}$$

(XVI.) (XVII.) (XVIII.)

$$\downarrow$$

$$\begin{array}{l}CO{\cdot}NH{\cdot}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H\\ CH_2 \quad CH_2{\cdot}SH\\ CH_2\\ CH{\cdot}NH_2\\ CO_2H\end{array}$$

(XIX.)

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[2] *J.*, 1935, 763; *A.*, 966.

[3] *J. Biol. Chem.*, 1929, **84**, 269; *A.*, 1929, 1491.

[4] *Ibid.*, p. 657; *A.*, 1930, 113.

[5] *Biochem. J.*, 1935, **29**, 1602; *A.*, 1110.

[6] *Ber.*, 1932, **65**, [*B*], 1192; *A.*, 1932, 935.

anhydride.[7] It gave the corresponding acid chloride (XVII) on treatment with phosphorus pentachloride, and this was coupled with cysteylglycyl ester to give the compound (XVIII). The purification of this substance was difficult, as was the hydrolysis of the ester linkage, which was finally accomplished in alkaline aqueous dioxan solution. Reduction of the resulting acid by means of phosphonium iodide gave the tripeptide γ-glutamylcysteylglycine (XIX) in small yield. The synthetic substance was identical in every respect with a sample of glutathione from natural sources.

Knowledge of the functions of glutathione in the living cell is still in an unsatisfactory state, though it is steadily increasing. (Sir) F. G. Hopkins and K. A. C. Elliott [8] found that fresh chopped liver, especially when obtained from well-fed animals, was capable of reducing glutathione, and that this property was largely lost if the tissue was heated at 52° for an hour. These results suggested that certain enzyme systems were concerned and that glutathione could act as a hydrogen carrier. P. J. G. Mann [9] found that glucose dehydrogenase reduced glutathione under anærobic conditions, and N. U. Meldrum [10] observed a reduction by intact mammalian erythrocytes in presence of glucose. Now, N. U. Meldrum and H. L. A. Tarr [11] have reported experiments showing that the isolated dehydrogenase system of Warburg and Christian reduces the oxidised peptide to the sulphhydryl form both anærobically and ærobically in the presence of hexosemonophosphoric acid, phosphohexonic acid, or fructosediphosphoric acid. When hexosemonophosphoric acid is being oxidised in the presence of molecular oxygen, the reaction velocity is roughly proportional to the concentration of glutathione, which is, therefore, acting as an oxygen carrier. *In vitro*, too, it has been stated by C. C. Palit and N. R. Dhar,[12] the oxidation of glucose by atmospheric oxygen at room temperature is induced by addition of glutathione. It is pointed out by N. U. Meldrum and H. L. A. Tarr that so far the only enzymes shown to be involved in glutathione reduction are intimately connected with carbohydrate oxidation.

It has, of course, been known for some time that glutathione is the co-enzyme of the glyoxalase system (G. E. Woodward [13] has recently based a method for the determination of glutathione on this fact) and again, glutathione is linked with carbohydrate metabolism. Experiments by R. Gaddie and C. P. Stewart[14] suggest that glutathione is concerned in the formation of methylglyoxal from carbohydrate, as well as in its conversion into lactic acid. As supporting the idea that glutathione is specially concerned in carbohydrate breakdown, both ærobic and anærobic, it is perhaps significant that K. Wachholder and W. Quensel[15] find the highest glutathione concentration in those muscles which are most often required for prolonged exercise, *e.g.*, the extensors used for maintenance of posture.

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[7] J. Melville, *Biochem. J.*, 1935, **29**, 179.

[8] *Proc. Roy. Soc.*, 1931, [*B*], **109**, 58; *A.*, 1931, 1182.

[9] *Biochem. J.*, 1932, **26**, 785; *A.*, 1932, 880.

[10] *Ibid.*, p. 817; *A.*, 1932, 880.

[11] *Ibid.*, 1935, **29**, 108; *A.*, 249.

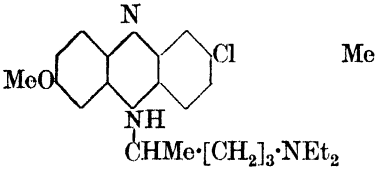
[12] *J. Indian Chem. Soc.*, 1934, **11**, 661; *A.*, 1934, 1314.

[13] *J. Biol. Chem.*, 1935, **109**, 1; *A.*, 784.

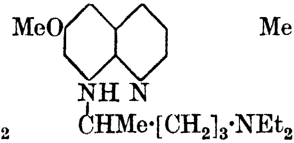
Chemotherapy.

Recent years have witnessed keen competition in matters of cost and efficiency between naturally occurring and synthetic drugs, the latter having the initial advantage of being in general much simpler in chemical constitution than the materials they are intended to supplement or supersede.

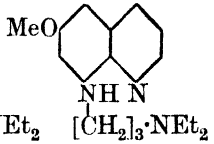
In the treatment of malaria interest has continued to centre round the relative merits of the I. G. Farbenindustrie A.-G. substances atebrin (XX) and plasmoquin (XXI),[16] the Russian product plasmocide * (XXII),[17] and the cinchona alkaloids, particularly quinine. The fact that plasmoquin is essentially antigametocidal in its mode of action and quinine and atebrin are primarily antischizonts[18] suffices to account for the continued investigation of the



(XX.)



(XXI.)



(XXII.)

[14] *Biochem. J.*, 1935, **29**, 2101; *A.*, 1278.

[15] *Pflügers Archiv*, 1934, **235**, 70; *A.*, 1935, 645.

[16] L. Knunjantz, *Bull. Acad. Sci. U.R.S.S.*, 1934, **8**, No. I, 153, 165; *B.*, 1935, 650; H. Mauss and F. Mietszsch, *Klin. Woch.*, 1933, **12**, 1276; P. Tate and M. Vincent, *Parasit.*, 1934, **26**, 523; E. J. R. MacMahon, *Brit. Med. J.*, 1934, 477; W. Schulemann, *Proc. Roy. Soc. Med.*, 1932, **25**, 897; *Ind. Med. Gaz.*, 1935, **70**, 83; W. Kikuth and F. Schonhofer, *Münch. med. Woch.*, 1935, **15**, 304; W. Kikuth, *Deutsche med. Woch.*, 1935, 573; C. D. Newman and B. S. Chalam, *Ind. Med. Gaz.*, 1935, **70**, 5; D. P. Williams and R. Battacharyya, *ibid.*, p. 8.

[17] E. Tarejew, *Bull. Soc. Path. exot.*, 1933, **26**, 1037; E. Tareer, *Med. Parasit. and Parasitic Dis.*, 1933, **2**, 189.

[18] F. M. Peter, *Trans. Roy. Soc. Trop. Hyg.*, 1935, **29**, 41.

* In all probability the methylene-bis-salicylate of (XXII) 6-methoxy-8-γ-diethylaminopropylaminoquinoline (Fourneau 710).

possibilities of the beneficial administration of plasmoquin or plasmocide in conjunction with quinine or atebrin.[19]

I. L. Kritschevski and A. I. Pines[20] have determined the concentrations of plasmoquin and plasmocide sufficient, when introduced into the Spinus-spinus at the height of infection with *Plasmodium præcox*, to destroy the power of the gametocytes to infect the *Culex pipiens*.

O. J. Magidson,[21] R. Robinson,[22] and their respective co-workers have attempted to correlate alterations in the alkoxy-radical and in the length and branching of the dialkylaminoalkyl side chain of 6-alkoxy-8-aminoquinoline derivatives of the plasmoquin type with the variations in antimalarial efficiency which accompany these changes in the structure of the molecule, and R. F. A. Altman,[23] in addition to working along similar lines, has considered changes in the structure of the natural alkaloid and finds that substitution in the $\mathrm{CH{\cdot}OH}$ and $\mathrm{CH{:}CH}$ groups of quinine destroys its antimalarial potency.

Preliminary reports on atebrin musonate,[24] a potential improvement on atebrin, are promising; I. L. Kritschevski and E. J. Stenberg[25] describe new derivatives of the plasmoquin type with chemotherapeutic indices greater than that of plasmoquin, but their true relative values have still to be established.

Serum therapy being as yet only partially successful in the treatment of pneumonia—F. Stein[26] has recently reported favourably on the combined effects of a serum and quinine—C. L. Butler, L. H. Cretcher, and their collaborators[27] have essayed to improve upon optochin (ethylhydrocupreine)[28] and report that hydroxy-ethylhydrocupreine affords considerable protection to infected mice in doses well below those at which toxic symptoms begin to manifest themselves. The most recent phase of their work makes contact with that of T. A. Henry, W. Solomon, and E. M. Gibbs,[29] who from their detailed study of the demethylation of quinine and quinidine conclude that Butler's α-apocupreine is identical with apoquinine and that his β-form is a mixture of apoquinine and a new alkaloid of lower rotation.

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[19] A. E. Eckhardt, *Arch. Schiff. Trop. Hyg.*, 1933, **37**, 223; P. F. Russell, *Arch. Int. Med.*, 1934, **53**, 309; W. H. W. Komp and H. C. Clark, *Amer. J. Trop. Med.*, 1935, **15**, 131; A. Krilow-Drenowsky, *Arch. Schiff. Trop. Hyg.*, 1935, **39**, 243; L. Robin and T. Van-Huan, *Bull. Soc. Path. exot.*, 1935, **28**, 650.

[20] *Klin. Woch.*, 1934, **13**, 807; 1935, **14**, 23; cf. W. Kikuth and F. Schonhofer, *ibid.*, 1934, **13**, 375.

[21] *Arch. Pharm.*, 1933, **271**, 359; 1934, **272**, 74; 1935, **273**, 320; *J. Gen. Chem. Russia*, 1934, **4**, 1047.

[22] *J.*, 1929, 2959, and subsequent papers; P. Tate and M. Vincent, *Parasit.*, 1933, **25**, 411.

[23] *Chem. Weekblad*, 1935, **32**, 345.

[24] J. R. Blaze and A. T. W. Simeons, *Ind. Med. Gaz.*, 1935, **70**, 185; E. P. Hicks, *Rec. Mal. Surv. India*, 1935, **5**, 203.

[25] *Z. Microbiol.*, 1935, **14**, 642.

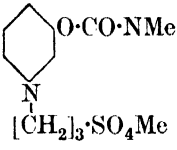
[26] *Münch. med. Woch.*, 1935, 1434.

[27] *J. Amer. Chem. Soc.*, 1935, **57**, 575, 738, 1083; W. W. G. Maclachlan, H. H. Permar, J. M. Johnston, and J. R. Kenny, *Amer. J. Med. Sci.*, 1934, **188**, 699.

[28] R. Morgenroth and co-workers, *Klin. Woch.*, 1911, **48**, 1560, 1979; 1914, **51**, 1829, 1865; *Deutsche med. Woch.*, 1914, **40**, 539; *Biochem. Z.*, 1917, **79**, 257; H. F. Moore, *J. Exper. Med.*, 1915, **22**, 269, 551.

It is rapidly becoming a recognised fact that quinine has definitely to compete not only with synthetic drugs but also with " totaquina " and like remedies,[30] hence the value as standards of reference of the carefully determined relative efficiencies in bird malaria of pure specimens of the principal cinchona alkaloids.[31]

With physostigmine (eserine) [32, 33] the position is much the same, the more simply constituted and less toxic synthetic drug prostigmine (XXIII) [34] rivalling it in efficacy. The investigations of M. Reinert and J. A. Aeschlimann [34] and the pioneer work in this field of E. Stedman,[35] and of E. and (Mrs.) E. Stedman,[36] the latter culminating in the production of myotin,[37] are jointly responsible for the introduction of prostigmine into medicine.[38] Its myotic action is less marked, its intestinal action much stronger, than that of physostigmine, and in therapeutic doses it lacks the instability and the toxic properties which detract from the value of the alkaloid.



(XXIII.)

The recent synthesis of *dl*-eserethole [33] suggests a near approach to the realisation of a cheap synthetic physostigmine, added interest being lent to this work by the markedly successful use of physostigmine, of prostigmine, and of the phenylmethylcarbamic ester derivative analogous to prostigmine in cases of myasthenia gravis,[39] the last-named remedy being effective despite its being the only one of the three drugs which does not act as an antidote to curare poisoning, whose symptoms closely resemble those of myasthenia gravis. The effect of injections of prostigmine and atropine sulphate can be observed within five minutes of administration, is marked within half an hour, but has unfortunately disappeared after about eight hours.

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[29] *J.*, 1934, 1923; 1935, 966; *Chem. and Ind.*, 1935, **54**, 641.

[30] E. J. Pampana and W. Fletcher, League of Nations Rep., 1934, **3**, 325; R. N. Chopra, B. Sen, and S. K. Ganguli, *Ind. Med. Gaz.*, 1935, **70**, 362.

[31] T. A. Henry, T. W. Trevan, and co-workers, *Biochem. J.*, 1934, 426. For a brief résumé see *Lancet*, 1935, ii, 631, or *Nature*, 1935, **136**, 539—a report of a chemotherapy discussion at the British Association Meeting, Sept. 9th, 1935.

[32] *Ann. Reports*, 1932, **29**, 197.

[33] P. L. Julian and J. Pikl, *J. Amer. Chem. Soc.*, 1933, **55**, 2105; 1934, **56**, 1797; 1935, **57**, 539, 563.

[34] *J. Pharm. Exp. Ther.*, 1931, **43**, 413.

[35] *Biochem. J.*, 1926, **20**, 719; 1929, **23**, 17.

[36] *J.*, 1929, 609.

[37] A. C. White and E. Stedman, *J. Pharm. Exp. Ther.*, 1931, **41**, 259.

[38] E. A. Carmichael, F. R. Fraser, D. McKelvey, and D. P. D. Wilkie, *Lancet*, 1934, i, 942.

[39] M. B. Walker, *ibid.*, p. 1200; E. A. B. Pritchard, *ibid.*, 1935, i, 432.

It is probable that the effective action of physostigmine and other urethanes in myasthenia gravis is due to the inhibiting action of these substances on the destruction of acetylcholine. In view of the suggestion of Loewi and Navratil [40] that such an explanation accounted for the action of physostigmine on the heart, and that the destroying agent was enzymic, E. Stedman and E. Stedman [41] investigated the effect on liver-esterase of a series of synthetic urethanes known to resemble physostigmine in other physiological properties. They found that these substances, in very low concentration, markedly inhibited the action of the esterase. The extension of these results to other esterases, with the demonstration that both pancreatic lipase and kidney phosphatase were relatively unaffected by urethanes,[42] was followed by experiments with acetylcholine as substrate and an attempt to purify the enzyme preparations—experiments which led E. Stedman, E. Stedman, and L. H. Easson [43] to the discovery of a specific " choline esterase." This enzyme rapidly hydrolysed esters of choline (acetylcholine most readily) and had little activity towards methyl butyrate (purified preparations recently obtained, 50—100 times as active towards choline esters as the original serum, had no detectable activity towards methyl butyrate [44]). Manometric methods for the estimation of choline esterase have been described by R. Ammon [45] and by E. Stedman and (Mrs.) E. Stedman.[46] It appears that the concentration of the enzyme in the blood varies considerably in different species, as also does its distribution between plasma and corpuscles.[46] It is absent from the cerebro-spinal fluid, but is present in brain, where the concentration in the basal ganglia is about double that in the cortex (Dikshit [47] has found a similar distribution of acetylcholine in brain).

Choline-esterase is inhibited by physostigmine and similar substituted urethanes to an even greater extent than liver-esterase, and the inhibiting power is proportional to the myotic activity.[48] A decrease in serum choline-esterase activity has been found by M. S. Jones and H. Tod [49] to follow administration of physostigmine (but not pilocarpine or adrenaline). It is thus reasonable to suppose that the remarkable effect of the urethane drugs in myasthenia gravis is related to their action on choline-esterase. The fault in this condition may, on this supposition, lie either in an excessive concentration of the enzyme or in a deficient production of acetylcholine. Stedman [50] has published figures indicating that in myasthenia gravis there is at any rate no increase in the blood choline-esterase, a result which, though not conclusive, suggests that the latter alternative is correct.

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[40] *Pflügers Archiv*, 1929, **214**, 678, 689.

[41] *Biochem. J.*, 1931, **25**, 1147; *A.*, 1931, 1190.

[42] E. Stedman and E. Stedman, *ibid.*, 1932, **26**, 1214; *A.*, 1932, 1166.

[43] *Ibid.*, p. 2056; *A.*, 1933, 315.

[44] *Ibid.*, 1935, **29**, 2563.

[45] *Pflügers Archiv*, 1934, **233**, 486; R. Ammon and G. Voss, *ibid.*, 1935, **235**, 393; *A.*, 1279.

[46] E. Stedman and E. Stedman, *Biochem. J.*, 1935, **29**, 2107.

[47] *J. Physiol.*, 1934, **80**, 409.

The year under review has seen an interesting addition to the means of combating infection of the urinary tract. Within the last four years good results in the treatment of urinary infections have been obtained by the use of a ketogenic diet,[51] *i.e.*, by a diet so poor in carbohydrate as to encourage the excretion of large amounts of acetoacetic and β-hydroxybutyric acids in a strongly acid urine. The effect was traced to the bacteriostatic action of β-hydroxybutyric acid.[52] M. L. Rosenheim [53] found that bacteriostatic power on the growth of *B. coli*, *in vitro*, was possessed by a number of other organic acids, notably benzoylacetic, β-hydroxypropionic, and lævulic. Mandelic acid compared favourably with β-hydroxybutyric acid, was non-toxic, was excreted unchanged in the urine, and was shown by clinical trial to be effective in cases of urinary infection, provided the urine was rendered strongly acid by administration of ammonium chloride. The claims of Rosenheim as to the therapeutic value of mandelic acid have been confirmed by D. M. Lyon and D. M. Dunlop.[54]

C. P. S.
J. S.

2. Plant Biochemistry.

Growth-regulating Substances.

The interest in these vital growth factors noted in the previous Report [1] continues steadily to increase. The notable work of F. Kögl and colleagues on the constitution of auxin-*A* and -*B* [2] has been followed by the isolation from urine and other sources of another substance exhibiting similar growth-stimulating properties, but quite unrelated, chemically, to the auxins. This "heteroauxin"[3] is identified as indole-3-acetic acid. It is produced by the bacterial decomposition of tryptophan, and according to Kögl, may occur in appreciable amounts in urine under conditions in which the bacterial population of the intestine becomes abnormal.

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[48] E. Stedman, private communication.

[49] *Biochem. J.*, 1935, **29**, 2242; *A.*, 1274.

[50] E. Stedman, *J. Physiol.*, 1935, **84**, 56 P.

[51] A. L. Clark, *Proc. Staff Meetings Mayo Clinic*, 1931, **6**, 605; H. F. Helmholz, *ibid.*, p. 609.

[52] A. T. Fuller, *Lancet*, 1933, i, 855.

[53] *Ibid.*, 1935, i, 1032; *A.*, 887.

[54] *Brit. Med. J.*, 1935, ii, 1096.

[1] *Ann. Reports*, 1934, **31**, 358.

[2] *Ibid.*, p. 216.

Although giving positive reactions in Went's auxin-*A* test (oat coleoptile), heteroauxin is conveniently differentiated from the auxins in routine laboratory work by being easily decomposed by acids and by its relative stability towards alkali. Auxin-*A* is readily decomposed by alkali, and auxin-*B* by both acid and alkali. Went's diffusion test records a molecular weight of approximately 175 as compared with approximately 350 for the auxins. On this basis the growth substance of coleoptile tips is definitely auxin-*A*, whereas that obtained from *Rhizopus* is or includes heteroauxin.

Physiological Activity of Growth Substance.—Although Kögl's work has given a definite chemical basis to the problem of growth substances, the response of plants to these substances demands, and is receiving, extensive investigation. Subsequently to the work previously reported,[4] R. Snow and B. Le Fanu[5] showed that pure auxin-*A* and also heteroauxin in concentrations of 1—2 p.p.m. induce strong cambial growth in strips of tissue from decapitated sunflower hypocotls. A. Uhrova[6] shows the growth-inhibiting substance present in leaves of *Bryophyllum crenatium* restricts the development of axial buds on that side of a shoot stump to which it is applied. He also confirms that the substance diffuses into the tissues and may subsequently be detected in the expressed juice and in an ethereal extract of the tissue. V. M. Katunski[7] records that auxin from coleoptile tips of oat and maize not only induces cell elongation in stems and checks the formation of adventitious rootlets on cut roots of *Vicia faba*, but also inhibits regenerative cell division in cut surfaces of succulent leaves. The "wound substance" appearing at the cut surfaces of decapitated roots is now assumed by F. Keeble and M. G. Nelson[8] to be auxin-*A*. The traumatic curvature of the root is explained by the effect of cutting on the distribution of auxin-*A* within it. No geotropic curvature occurs in the root until an adequate amount of auxin-*A* has been acquired. The distinction is made between the effects of auxin in promoting growth (controlled by concentration) and in inducing curvature, which depends on the gradient of concentrations on opposite sides of the root.

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[3] F. Kögl and D. G. F. R. Kostermans, *Z. physiol. Chem.*, 1934, **228**, 90 104, 113; *A.*, 1934, 1418.

[4] *Ann. Reports*, 1934, **31**, 359.

[5] *Nature*, 1935, **135**, 149; *A.*, 418; R. Snow, *ibid.*, p. 876; *A.*, 905.

[6] *Planta*, 1934, **22**, 441; *A.*, 1935, 548.

[7] *Compt. rend. Acad. Sci. U.S.S.R.*, 1935, **1**, 661; *A.*, 795.

[8] *Proc. Roy. Soc.*, 1935, [*B*], **117**, 92; *A.*, 548; cf. *New Phytol.*, 1930, **29**, 289.

Another form of activity of a growth-regulating substance is postulated by J. P. McCollum,[9] who ascribes the general retardation of vegetative growth in plants during the development of fruits to the presence in the fertilised ovary of auxin or a related substance. N. Cholodny [10] demonstrates the existence of a growth-substance in the starchy endosperm of maize and other *Gramineæ* in the very early stages of germination. Its formation is associated with starch hydrolysis, and probably begins with the onset of enzyme activity following the first absorption of water by the seeds. It is not initiated by the germinative process, since it occurs in seeds which have lost, naturally or artificially, their germinative power. Once formed, the growth substance passes rapidly into the developing embryo.

Callus formation on cut epicotls following the application of growth substance from pollen and urine in the form of a lanoline paste is further examined by F. Laibach and O. Fischnich,[11] who have now developed a method of determining the activity of auxin preparations, depending on the rate of thickening of decapitated epicotls of *Vicia faba*. Standard curves representing the relationship between the percentage increase in diameter of the epicotl and the concentration of growth substance applied are obtained by means of heteroauxin pastes containing 73×10^{-6} g. of β-indolylacetic acid per g. of paste. In a subsequent paper [12] the same authors record the root-initiating effects of pure heteroauxin. Treatment of intact stems with the paste results in a callus formation at or near the point of application, followed, in a few days, by the appearance of rootlets. Application to the upper side of the mid-rib of a leaf results in relatively greater growth on that side, causing a local thickening of the leaf and a downward curvature. Callus or root formation on the leaf-stalk, if occurring at all under these conditions, is slight or late in developing. If, however, the underside of the mid-rib is treated, the leaf-stalk swells, and on the sides of the stem lying beneath the leaf pair a callus is produced, followed by a line of rootlets. On the other sides of the stem neither callus nor roots appear. With a less concentrated paste, the rootlets are formed more slowly, principally at the upper end near the callus.

[9] *Cornell Univ. Agric. Exp. Sta. Mem.*, 1934, No. 163, 27 pp.; *A.*, 1934, 1419.

[10] *Planta*, 1935, **23**, 289; *A.*, 905.

[11] *Ber. deut. bot. Ges.*, 1935, **53**, 469; *A.*, 1039.

[12] *Ibid.*, p. 495; *A.*, 1038.

When stems are placed horizontally, roots are formed principally on the under side. From these and numerous other results Laibach suggests that the root-stimulating substance moves axially within the plant tissues, mainly through the large conducting vessels. Transverse movement is probably a much slower process. Hetero-auxin thus appears to possess the cell-elongating influence formerly attributed to auxin-*A*, together with a root-initiating power. Which of these two functions becomes dominant depends on the conditions of the experiment, the manner of application, and the quantity of the growth-substance concerned. Thimann [13] compares the root-forming properties of indole-3-acetic acid with those of the root-hormone previously examined [14] and concludes that the growth-promoting and the root-forming substance are identical. A. T. Czaja [15] differentiates between the action of growth substance on decapitated stems when applied in the direction of normal movement within the plant (axially), and when applied transversely. The former leads to lengthening but no thickening of the stem, the latter restricts stem growth and induces a widening and possibly shortening of the cells and thickening of the stem below the point of application. The latter is explained as the result of an antagonism between the natural and the induced stream of growth-substance within the plant. Positive curvature may be induced by transverse application of a concentrated preparation of growth-substance and is attributed to partial transverse streaming. Czaja holds that the primary function of the growth substance is the stimulation of cell elongation but not of division, and that the latter, when it occurs, is a secondary effect resulting from localised disturbance of the polarity of the plant system. The growth substance is assumed to polarise plant cells. According to Laibach (*loc. cit.*) high concentrations of growth substance cause positive curvature of stems through cell injury in the treated tissue.

From the physiological viewpoint the activities of growth hormones appear to have been somewhat clarified, although opinion as to the mechanism of their action is still divided. It is, however, not yet clear, on chemical grounds, why the auxins and hetero-auxin should possess such functional similarities.

Possible Constitutional Specificity of Growth Substances.—It has been anticipated by a number of workers in this field that the activity of these substances might be associated with some particular molecular structure or with a specific grouping of atoms within the molecule. Physiological activity was thought to be related to the position of the unsaturated linking. Hydrogenation of auxin-*A* leads to complete loss of hormonal activity, as also does esterification. Heteroauxin similarly loses its activity on hydrogenation, but certain esters and a number of simple derivatives are active, although possessing potencies less than that of the parent substance. Relationships between constitution and growth-regulating properties are, however, not yet very clear. For instance, Kögl [16] finds that the activity of esters of indole-3-acetic acid varies in the order Me $>$ Et $>$ Pr^{α} $>$ Pr^{β}. Among chemically related substances examined, Kögl [17] demonstrated the activity of :

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[13] K. V. Thimann and J. B. Koepfli, *Nature*, 1935, **135**, 101; *A.*, 418.

[14] K. V. Thimann and F. W. Went, *Proc. K. Akad. Wetensch. Amsterdam*, 1934, **317**, 457; *A.*, 1934, 1418.

[15] *Ber. deut. bot. Ges.*, 1935, **53**, 197, 221, 478; *A.*, 672, 1039.

1-Methylindole-3-acetic acid (ethyl ester inactive).
2-Methylindole-3-acetic acid (methyl ester inactive).
5-Methylindole-3-acetic acid (methyl ester active).
Indole-3-pyruvic acid.
Indole-3-α-propionic acid.

On the other hand, the following proved inactive :

Dihydroindole-3-acetic acid.
2-Ethylindole-3-acetic acid.
2 : 5-Dimethylindole-3-acetic acid.
l- and *r*-Indole-3-lactic acids.
Indole-2- and -3-carboxylic acids.
Indole-3-β-propionic acid.

A. E. Hitchcock [18] increased the list of active substances by the addition of indole-3-*n*-propionic, phenylacrylic, and phenylpropionic acids, with the aid of which he induced root-initiation, bending and intumescence of stems, and epinasty of leaves. Although these experiments may not be dealing with quite the same phenomena, they recall earlier work of Zimmerman and others [19] of the same institution, in which exposure of plants to appropriate concentrations of carbon monoxide checked stem elongation, caused leaf epinasty, and induced the development of axial buds and of adventitious roots. Similarly [20,21] ethylene, propylene, butylene, and acetylene were found to cause epinasty in intact or excised petioles and by repeated treatment produced root formation on stems and curvature in roots. Recently F. W. Zimmerman and F. Wilcoxon [22] have shown that α- and β-naphthyl-, acenaphthyl-5-, phenyl-, fluorenyl-, and anthracyl-acetic acids, indolebutyric acid, and α-naphthylacetonitrile exhibit the general physiological activities of growth substances. The close similarity between the effects of ethylene and of growth substances on plants is discussed in a further paper [23] in which the significance of observations of the emanation of gas resembling ethylene from certain plant tissues [24] is emphasised. In this connection the action of growth substances in increasing these emanations from treated plants (Zimmerman and Wilcoxon, *loc. cit.*) is worthy of note.

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[16] *Z. physiol. Chem.*, 1935, **235**, 181, 201; *A.*, 1351.

[17] *Loc. cit.*, also F. Kögl, A. J. Haagen-Smit, and H. Erxleben, *ibid.*, 1934, **228**, 90; *A.*, 1934, 1418.

[18] *Contr. Boyce Thompson Inst.*, 1935, **7**, 87; *A.*, 795.

[19] P. W. Zimmerman, W. Crocker, and A. E. Hitchcock, *ibid.*, 1933, **5**, 1, 195; *B.*, 1933, 726; *A.*, 1933, 437.

[20] W. Crocker, P. W. Zimmerman, and A. E. Hitchcock, *ibid.*, 1932, **4**, 177; *A.*, 1932, 890.

[21] *Idem*, *ibid.*, 1933, **5**, 351; *B.*, 1933, 1027.

Such investigations widen our conception of growth-regulating substances to an almost bewildering extent. The hitherto popular belief in specific regulatory action becomes increasingly difficult to maintain. On the other hand, it may be questioned whether the so-called growth substances are really the active agents, or whether, within the plant system, they may give rise to other regulatory agents, not yet isolated, among which the anticipated specificity may yet be established. The work of the Boyce Thompson Institute seems to point to ethylene as being likely to be concerned in this respect. The experimental difficulty of subjecting plants to the action of ethylene under conditions comparable with that of the various growth substances has been pointed out, and tends to retard the elucidation of closer relationships.

Growth Substances and the Lower Organisms.—Continuing his earlier work,[25] W. H. Schopfer now shows [26] that the thermostable auxin-like factor isolated from wheat germ,[27] rice polishings,[28] urine,[29] and flower stamens,[30] which promotes vegetative growth and zygote formation in *Phycomyces*, may be synthesised by the organism itself, provided that vitamin-B_1 is supplied in the nutrient.[31] That the growth factor itself is not vitamin-B_1 is shown by its ability to activate yeast and its relative insolubility in chloroform.[32] This auxogenic action of vitamin-B_1 is apparently favoured by a generous supply of nitrogen in the nutrient medium and is most marked at p_H 7·0—7·2.[33] Synthesis of growth substance by the auxoheterotrophic *Phycomyces* in vitamin-free media may be initiated by inoculation with extracts of cultures grown on active media, or with cultures of auxoautrotrophic organisms, *e.g.*, *Mucorineæ*, on vitamin-free media. Both sources can also stimulate yeast cultures.[34] Spores of *Phycomyces* apparently contain sufficient of the growth factor for germination, but external activation is necessary for further development.[35]

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[22] *Contr. Boyce Thompson Inst.*, 1935, **7**, 209.

[23] W. Crocker, A. E. Hitchcock, and P. W. Zimmerman, *ibid.*, p. 231.

[24] F. E. Denny and L. P. Miller, *ibid.*, p. 97; *A.*, 1179.

[25] *Ann. Reports*, 1934, **31**, 366.

[26] *Compt. rend.*, 1934, **199**, 1656; *A.*, 1935, 156.

[27] *Arch. Sci. phys. nat.*, 1934, [v], **16**, Suppl., 47, 165; *A.*, 1935, 663.

[28] *Arch. Mikrobiol.*, 1934, **5**, 502, 511; *A.*, 1935, 534.

[29] *Arch. Sci. phys. nat.*, 1934, [v], **16**, Suppl., 200; *A.*, 1935, 786.

[30] *Ibid.*, p. 169; *A.*, 1935, 663.

[31] *Compt. rend.*, 1935, **200**, 1965; *A.*, 1027.

[32] *Arch. Sci. phys. nat.*, 1935, [v], **17**, Suppl., 56; *A.*, 1289.

Further examination of the growth substance of yeast is recorded by R. J. Williams and D. H. Saunders.[36] A more highly purified preparation of pantothenic acid[37] is obtained and its activity shown to be intensified by the presence of bios I (inositol), and of vitamin-B_1, minute amounts of the latter producing very marked effects. Pantothenic acid is regarded as the principal constituent of bios. It appears also to be closely related to " biotin," isolated from bios II from yeast and from egg yolk by Kögl.[38] Biotin is regarded in some quarters as the active agent stimulating cell division. A. J. Salle and R. W. Dunn[39] describe a growth factor, isolated from rice bran, which stimulates growth and the production of acid and gas from carbohydrates by a number of species of bacteria. Organisms which do not ferment carbohydrates are unaffected in any way by this factor, which is probably pantothenic acid. Nodule organisms also contain pantothenic acid, which appears to pass from the bacteria into the host plant, the growth of which is also influenced. The acid does not affect the actual fixation of nitrogen directly, but is an important secondary factor as a result of its action on carbohydrate anabolism.[40] That the active principle of bios is freely distributed in the animal world and is particularly concentrated in the kidneys and in tumour growths is shown by C. Dittmar.[41]

Hardiness and Drought Resistance in Plants.

The chemical and physical changes occurring during the freezing of plant tissue have formed the subject of considerable enquiry in recent years, more especially since it has been recognised that the part played by manurial treatment in modifying the frost resistance of plants is a very definite one. Among others, F. Schaffnit and A. F. Wilhelm,[42] working with stored potatoes, tomatoes, and various cereal crops, confirm a number of earlier observations that generous manuring with potassium salts increases cold resistance and further demonstrates that growth in nitrogen- or phosphate-deficient soils produces a somewhat similar effect. Possible correlation between frost resistance and the concentration of cell saps is also examined. Although the sugar content of saps tends generally to be high in more resistant samples, no definite relationship is apparent. Neither the reaction of the sap, its dry matter content, nor its osmotic pressure seems to be an influential factor in this respect. It is also shown that freezing for a short time at a very low temperature produces effects different from those resulting from exposure to milder freezing for a longer time. Similar results are recorded by A. Anderson and T. A. Kiesselbach,[43] with the further observation that in wheat plants the rates of fall and of subsequent rise in temperature contribute materially to the severity of the injury produced. In a later publication Wilhelm,[44] using rape and spinach plants, and following up earlier indications that cell protein was the seat of cold injury, compared the protein content of plants in relation to hardiness, but failed to establish that the two factors were interdependent. The freezing of plant proteins is shown by Tadokoro and Joshimura [45] to result in an increase in amino- and amide-nitrogen, histidine and arginine, and a decrease in tyrosine fractions. Wilhelm (*loc. cit.*) indicates, however, that no parallelism exists between protein breakdown and frost resistance. It is suggested that the effects of manuring on hardiness appear more likely to be related to variations induced in the phosphatide content. The favourable effect of potash manuring is attributed in part to its action in increasing sap concentration and in part to a more specific effect on the physical condition of the cell colloids. It is further recorded that the decline in sugar content during exposure to cold is slower in nitrogen- and potassium-deficient plants than in those more adequately nourished. A possible protective action of sugar against injury to cell contents is indicated. In this connection the observation of K. Böning and E. Böning-Seubert [46] that deficient salt nutrition tends to lower the sugar content of plants is significant. The influence of sugar on frost resistance has also been investigated by Newton and colleagues,[47] who show that freezing (at − 7°) of the expressed juice of unhardened wheat plants results in the precipitation of proteins, the extent of which is lowered by additions of sucrose or glucose in amounts up to 8% of the juice. The "salting-out" of proteins and their coagulation by acids or bases are also restricted by the presence of sucrose. On the other hand, removal of electrolytes from the juice (by dialysis) increases the amount of protein precipitated by freezing. In a subsequent publication [48] these effects are shown to be accompanied by an increase in amino-nitrogen and in the sensitivity of the protein to hydrolysis by alkali. Again the changes are lessened by additions of sugar. The opinion is expressed that protein degradation in hardened plants is due to frost action and is not a protective adaptation.

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[33] *Arch. Mikrobiol.*, 1934, **5**, 502, 511; *A.*, 1935, 534.

[34] *Ibid.*, 1935, **6**, 196; *A.*, 1167.

[35] *Ber. deut. bot. Ges.*, 1935, **53**, 466; *A.*, 1039.

[36] *Biochem. J.*, 1934, **28**, 1887; *A.*, 1935, 124.

[37] *Ann. Reports*, 1934, **31**, 365.

[38] *Ber.*, 1935, **68**, [*A*], 16; *A.*, 418.

[39] *Proc. Soc. Exp. Biol. Med.*, 1934, **32**, 168; 1935, **32**, 939; *A.*, 1935, 408, 1419.

[40] C. H. McBurney, W. B. Bollen, and R. J. Williams, *Proc. Nat. Acad. Sci.*, 1935, **21**, 301; *A.*, 1167.

[41] *Biochem. Z.*, 1935, **279**, 99; *A.*, 1165.

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[42] *Phytopath. Z.*, 1933, **25**, 266; *B.*, 1933, 643.
[43] *J. Amer. Soc. Agron.*, 1934, **26**, 44; *B.*, 1934, 418.
[44] *Phytopath. Z.*, 1935, **8**, 111; *B.*, 1061.
[45] *J. Fac. Agric. Sapporo*, 1928, **25** (cited by Wilhelm).
[46] *Biochem. Z.*, 1934, **270**, 122; *A.*, 1935, 708.

If sugar is to be regarded as a protective agent against injury by cold, the respiratory exchange at low temperatures, in so far as it affects sugar contents, might be expected to show some relationship to hardiness. On this point R. Newton and J. A. Anderson [49] report that the respiration rates of spring and winter wheats in the pre-hardened condition are identical. As hardening proceeds, however, the rates decline, those of the hardier winter varieties reaching a lower level than those of spring types. The catalase activity of wheat leaves, examined in autumn, is found to be closely related to the winter hardiness of different varieties.[50] In the course of a general investigation of this subject S. T. Dexter [51] reports that the respiration rates of wheat and cabbage seedlings stored at 2° decrease continuously irrespective of their relative hardiness or the extent of the increase in their sugar contents. The oxidase activity of plants is not affected at this temperature. Catalase activity in cabbage is also unchanged whether plants are hardened in light or in darkness. Under both conditions the degree of hardening is considerable. The catalase of the wheat plants at 2° increases in darkness but decreases in light. It is concluded that neither respiratory rates nor enzymic activity can be directly associated with the hardening process. Dexter [52] also confirms that, whereas cabbage and winter cereals having low nitrogen and high carbohydrate contents harden satisfactorily at 2°, high-nitrogen wheat fails to do so at this temperature. He also shows that increases in soluble nitrogen in the plants follow low-temperature storage whether hardening occurs or not. Thus, while there is a general association between hardiness, low respiration rates, high sugar content, and increased soluble nitrogen, it cannot be said that the last-named three factors, individually or collectively, are essential characteristics of hardiness.

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[47] R. Newton and W. R. Brown, *Canadian J. Res.*, 1931, **5**, 87; *A.*, 1931, 1198.

[48] R. Newton, W. R. Brown, and J. A. Anderson, *ibid.*, p. 327; *A.*, 1931, 1465.

[49] *Ibid.*, p. 337; *A.*, 1931, 1465.

[50] R. Newton and W. R. Brown, *ibid.*, p. 333; *A.*, 1931, 1465.

[51] *Plant Physiol.*, 1934, **9**, 831; *A.*, 1935, 263.

[52] *Ibid.*, 1935, **10**, 149; *A.*, 904.

The balance of " free " and " bound " water in plant colloidal systems has, from time to time, been suggested as a basis for the consideration of frost resistance. Using calorimetric methods for determining the extent of ice formation in plant tissues, Dexter [53] has re-examined the problem from this point of view. Repeated freezing and thawing (at intervals) of crowns of wheat plants shows that water separated from the colloids as ice during freezing is not completely reabsorbed on subsequent thawing, *i.e.*, the process is not completely reversible. A repetition of the freezing process results in the formation of a larger amount of ice. As the plants harden in the field, the difference between the amounts of unfrozen water at the first and second and subsequent freezings steadily declines. There is, therefore, a steady approach to complete reversibility of ice formation with increasing hardiness. The proportion of bound (unfrozen) water in the plant tissue falls as the temperature of freezing is lowered, presumably as the result of the " freeing " of bound water. The proportion of unfrozen water in hardy varieties is greater than that in more tender plants. On the other hand, the amount of unfrozen water per gram of dry matter at the first freezing (− 7°) is higher in unhardened plants, but differences between hardened and tender plants in this respect practically disappear at a second freezing. It is implied that, although hardening does not definitely increase the hydration of plant colloids, the condition of hydration is made a more stable one.

As the hardening of wheat plants proceeds, there is a steady decrease in the amount of extractable electrolytes in the crown and root tissues, and in the concentration of salts in the unfrozen water, values for hardier varieties being somewhat lower throughout. This observation falls into line with the influence of manuring on hardiness in so far as low levels of nutrition induce low soluble-salt concentrations in the plants. It is also significant that nitrogen-deficient plants exposed to low temperatures in darkness showed the characteristic decrease in electrolyte content and became hardened, but high-nitrogen plants under the same condition neither hardened nor showed a loss of soluble salt content. Conditions in lucerne

[53] *Plant Physiol.*, 1934, **9**, 601; 1935, **10**, 403; *A.*, 1935, 266, 1288.

roots appear to be somewhat different. For example, the percentage of dry matter does not increase during exposure to cold and there is no decrease in the soluble electrolyte content. Nevertheless the salt concentration of the unfrozen water in hardened plants is less than that of unhardened controls, although the difference is less definite than in the case of wheat. This is perhaps to be associated with the fact that a much greater degree of hardness (*i.e.*, resistance to lower temperatures) is attainable in wheat than in lucerne. H. M. Tysdal,[54] in an examination of lucerne, records that diastatic activity of leaves is unrelated to hardiness, but that roots of the hardier varieties are enabled to accumulate relatively more sugar in the autumn. An examination of wheat leaves following low-temperature exposure reveals [55] a general increase in the osmotic pressure and in the total dry matter and sugar contents of the sap. Differences in these values for varieties of different hardiness are, however, small. Although the general trend in important changes during hardening may be indicated by the leaves, comparison with Dexter's work suggests that the elucidation of the chemistry of frost resistance is to be sought in the crown and root system.

Much less detailed attention has been given to the problem of drought resistance, but there is evidence that here again the bound water of the plant system is a vital factor. R. Newton and W. M. Martin [56] have established a cryoscopic method for determining the bound water in colloidal systems by the aid of which they show that in wheat and in grasses the bound water content of the expressed sap of leaves is a satisfactory measure of the adaptability of the plants to drought conditions. That drought resistance may be influenced by manuring is indicated by N. L. Udolskaja,[57] who records that treatment of black-earth soils with sodium phosphate in conjunction with calcium nitrate increases the water-retaining capacity of certain plants and permits a suitable, though reduced, water balance to be maintained during the dry season. The beneficial effects of phosphate manuring in this respect are also reported by Antonov *et al.*[58] and by S. P. Molchanov and A. A. Shirshov,[59] who find that, although chemical fertilisers do not affect the general course of water-evaporation curves of plants and that potassium

[54] *J. Agric. Res.*, 1934, **48**, 219; *B.*, 1935, 644.

[55] E. Constantinescu, *Planta*, 1933, **21**, 304; *A.*, 1934, 464.

[56] *Canadian J. Res.*, 1930, **3**, 336; *A.*, 1931, 534.

[57] *Compt. rend. Acad. Sci. U.S.S.R.*, 1934, **2**, 45; *A.*, 1935, 821.

[58] L. I. Antonov, K. A. Kaltschevski, A. M. Ruguzov, K. N. Faktulin, and T. G. Katarian, *North Caucasian Grain Inst. Coll. Sci. Papers*, 1933, No. 1, 142; *B.*, 1935, 37.

[59] *Chem. Social Agric.*, 1932, **1**, No. 1, 82; *B.*, 1935, 215.

salts do not afford any protection against drought, nitrogenous and phosphatic fertilisers tend to lower the water consumption per unit of dry matter produced by the plants. R. F. Williams[60] confirms the effect of moderate supplies of phosphates on transpiration ratios, but shows that the action of phosphate is a limited one.

Carbohydrate changes are also concerned in the conditioning of plants to resist drought. Drought-hardening may be effected by maintaining plants with a lowered water supply until the leaf tips begin to die back. During this period I. M. Vassiliev and N. G. Vassilieva[61] observe a steady increase in the monosaccharide, a variable change in the sucrose, and, after a preliminary fall, a considerable and sustained rise in hemicellulose content. Subsequent watering of the treated plants results in a delayed increase in the sucrose content to values which ultimately exceed those in untreated controls. Plants thus conditioned have a permanently lowered water content. It is also recorded[62] that drought resistance may be increased by soaking partly germinated seeds in twice-molar solutions of sugars for 6 days.

Thus, while much yet remains to be investigated, it would appear that the water relationships of plant colloids are a dominant factor in both frost- and drought-resistance. Carbohydrate materials represent important agents protecting the colloidal system from physical denaturation and probably also, in the case of frost resistance, from chemical decomposition in which protein constituents are largely concerned.

Plant Nutrients.

Nitrogen.—A considerable proportion of a wide literature concerning plant nutrition is occupied with the question of nitrogen. In a number of papers dealing with the complex problem of the comparative values of nitrates and ammonium salts for this purpose, the influence of the level of supply of other nutrient materials receives rather more prominence this year. The utilisation of ammonium salts by the cotton plant under acid conditions is shown by V. S. Ivanova[63] to be favoured by the presence of calcium chloride or sulphate but adversely affected by that of magnesium chloride or sulphate. Salts of potassium do not affect the intake of either ammonia or nitrates under acid conditions but increase that of nitrate from neutral media. In spite of the influence of these other nutrient materials the relative assimilation of the two forms of nitrogen still appears to depend mainly on the reaction of the substrate. As a complementary observation to the above may be cited the restriction of the intake of potassium in the presence of sodium nitrate.[64] According to I. G. Dikusar [65] the beneficial effect of ammonium chloride on the growth of flax in sand cultures is increased by raising the concentration of calcium and magnesium in the nutrient. In agreement with Ivanova's observations (above) a high proportion of magnesium without adequate amounts of calcium is shown to produce adverse effects. Ammonium-nutrition tends to lower the base (notably K) and increase the phosphate contents of plants, whereas nitrates have the opposite effect. Working with sugar beet, A. V. Vladimirov [66] compares the influence of chlorides and of sulphates on the utilisation of nitrogen in sand cultures. With nitrogen supplied as ammonium salts, chlorides produce the higher yield of beet, but with nitrates the best results are obtained by use of sulphate-containing nutrients. With increasing concentrations of ammonium salts in media having p_H 4·5 and 6·5 there is a steady rise in the nitrogen content of the crop whether sulphate- or chloride-nutrients are used. The effect is reversed in media having p_H 8·2. The soluble-nitrogen content of the beet is increased by potassium chloride but lowered by the sulphate. By raising the level of supply of potassium in either form, the total nitrogen and sugar content of the plants is increased in nutrients of p_H 4·5 and 8·2 but unaffected by those having p_H 6·5. The percentage of sugar in beet from nitrate media is higher when sulphates than when chlorides are given. At all p_H levels potassium salts increase the chlorophyll content of leaves of plants grown in ammonium-media. The individual effects of differences of reaction and of the composition of other solutes present tend in general to be superimposable. Another instance of this generalisation is afforded by S. F. Trelease and H. M. Trelease,[67] who show that the growth of plants tends to lower the p_H of nutrient solutions in which the $NO_3 : NH_3$ ratio is low and to increase the p_H when the ratio is high. Suitable adjustment of the ratio forms the basis of a method, devised by these authors, for preparing media which, in use, retain the initial p_H for a number of days.[68]

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[60] *Austral. J. Exp. Biol.*, 1935, **13**, 49; *A.*, 795.

[61] *Bull. Acad. Sci. U.S.S.R.*, 1934, 1340; *A.*, 1935, 796.

[62] M. T. Timofeeva, *Plant Ind. U.S.S.R.*, 1933, *A.*, No. 7, 69; *A.*, 1935, 1045.

[63] *Lenin Acad. Agric. Sci. Ged. Inst. Fert.*, 1934, No. 3, 77; *B.*, 1935, 918.

Potassium.—Further evidence is recorded of the comprehensive character of the various effects of potassium in the intake and utilisation of other nutrients. In connection with the manuring of cereals it is shown that potassium sulphate increases the total- and phytin-phosphorus and protein content of wheat, although in the matured plants the amount of potassium in the tissues is not greatly affected.[69] The reciprocal effects of potassium and nitrogen on the assimilation, transpiration, and chlorophyll content of rye are examined by G. Gassner and G. Goeze.[70] Maximum assimilation occurs with moderate nitrogen supplies and small proportions of potassium, or with excessive nitrogen and high potassium supplies. With adequate amounts of potassium, increasing supplies of nitrogen increase assimilation and transpiration, whereas in potassium deficiency the reverse occurs. Under both sets of conditions the chlorophyll content of the plants is increased. According to G. Rohde [71] the action of potassium in increasing ærobic and retarding anærobic respiration in plants is related to its ability to improve the distribution of iron within the system. In tomato plants insufficiency of potassium lowers the ash content of the dry matter and increases the proportion of calcium, magnesium, and phosphorus therein.[72] The question of the possible replacement of potassium by other bases in respect of its function within the plant continues to be a subject of investigation. A. G. McCalla [73] provides further confirmation that in the wheat plant potassium deficiency may be partly counteracted by a suitable supply of sodium. M. Korczewski and F. Majewski [74] indicate that the sodium requirement of oats in relation to dry matter production varies considerably with the season, values ranging from 22 to 74% of the requirement of potassium. Although the growth of plants is greatly influenced by the supply of sodium, the amount remaining in the plant at maturity is very small, none occurring in leaves. A number of attempts to discover whether rubidium, cæsium, or lithium can play the part of potassium in the plant system have in practically all cases shown negative results.[75] Rubidium is taken up by plants and tends to modify mineral metabolism. Only in one instance is it shown that potassium can be partially replaced by rubidium, *viz.*, in the marine diatom *Witzschia closterium*.[76] K. Scharrer and W. Schropp [77] record stimulative effects of small concentrations of lithium, but there is no evidence that the action of the base bears any resemblance to that of potassium.

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[64] J. Mikulowski-Pomorski and J. Salcewicz, *Rocz. Nauk. roln. leśn.*, 1934, **31**, 116; *B.*, 1935, 966.

[65] *Lenin Acad. Agric. Sci. Ged. Inst. Fert.*, 1934, No. 3, 67; *A.*, 1935, 1178.

[66] *Ibid.*, 1934, No. 3, 104; *B.*, 1935, 868.

[67] *Amer. J. Bot.*, 1935, **22**, 520; *A.*, 1178.

[68] *Science*, 1933, **78**, 438; *A.*, 1934, 120.

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[69] L. Marimpietri, *Ann. R. Staz. Chim. Agrar. Sperim.*, 1934, **14**, No. 313; *B.*, 1935, 73.

[70] *Z. Pflanz. Düng.*, 1934, *A*, **36**, 61; *B.*, 1935, 72.

[71] *Ibid.*, 1935, **39**, 159; *A.*, 1178.

[72] T. G. Phillips, T. O. Smith, and R. B. Dearborn, *New Hamps. Agric. Exp. Sta. Tech. Bull.*, 1934, No. 59; *A.*, 1935, 553.

[73] *Canadian J. Res.*, 1934, **11**, 687; *B.*, 1935, 244.

[74] *Rocz. Nauk. roln. leśn.*, 1934, **31**, 22, 141; *B.*, 1935, 966, 967.

[75] W. E. Brenchley, *Ann. Appl. Biol.*, 1934, **21**, 398; *A.*, 1934, 1274; F. Alten and R. Gottwick, *Ernähr. Pflanze*, 1933, **29**, 393; *B.*, 1934, 33; K. Heller, K. Peh, and F. Gürtler, *Z. Pflanz. Düng.*, 1934, [*A*], **35**, 215; *B.*, 1935, 1113.

Secondary Nutrients.—A number of workers record beneficial effects on plant growth of mixtures of the secondary or " micro "-nutrients added to water-culture media, in comparison with those in which highly purified salts have been used to provide the major nutrients. The elements commonly shown to exert secondary effects include copper, aluminium, manganese, zinc, boron, fluorine, and iodine. In the case of flax, A. P. Schtscherbakov [78] shows that such a mixture of nutrients not only increased the total growth, but caused greater chlorophyll accumulation, increased the percentage of calcium and magnesium in the dry matter of leaves, and decreased that in the stems. Differences in the distribution of mineral matter, notably calcium and magnesium, in the plant due to the presence of the " micro-"elements are attributed to differences in the form of combination in the tissues. Organic compounds predominate in the presence, and inorganic compounds in the absence, of these elements. R. S. Young,[79] working on somewhat similar lines and using green algæ as test plants, reports that no relationships are apparent between the toxic or stimulative action of a number of the rarer elements in soils and the oxidation–reduction potential of the growth media.

Among more detailed examinations of the individual elements may be cited those dealing with the function of manganese in plant growth. In certain *Coniferæ*, N. C. Nag [80] observes a marked increase in manganese content during the formation of the female flowers. Cones also have a relatively large proportion of manganese. K. Scharrer and W. Schropp [81] show that, in sand cultures of cereals, replacement of the customary amounts of iron in the media by manganese (up to 50%) tends to increase root production at the expense of shoot growth. Complete replacement prevents growth. The intake of manganese by wheat seedlings is apparently influenced to a large extent by the nature of the anions present, as well as by the reaction of the medium.[82]

Interdependence of the copper and iron functions in plants is indicated by L. G. Willis and J. R. Piland,[83] who record that accumulations of iron in maize plants grown under certain conditions and formerly ascribed to deficiency of potassium, may be corrected and the crop yield increased by application of copper sulphate to the soil. Further,[84] in orange trees suffering from a form of chlorophyll deficiency, treatment with copper salts produced a marked increase in chlorophyll production, although no copper actually accumulated in the leaves.

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[76] F. A. Stanbury, *J. Marine Biol. Assoc.*, 1934, **19**, 931; *A.*, 1934, 821.

[77] *Ernähr. Pflanze*, 1933, **29**, 413; *B.*, 1934, 417.

[78] *Z. Planz. Düng.*, 1935, **39**, 129; *A.*, 1179.

[79] *Cornell Univ. Agric. Exp. Sta. Mem.*, 1935, No. 174; *B.*, 1109.

[80] *Trans. Bose Res. Inst.*, 1932—1933, **8**, 179; *A.*, 1935, 266.

[81] *Z. Pflanz. Düng.*, 1934, *A*, **36**, 1; *B.*, 1935, 73.

[82] J. Davidson, *Proc. 2nd Internat. Congr. Soil Sci.*, 1933, **2**, 84; *A.*, 1934, 337.

The ill effects of boron deficiency on growth and disease in plants have been sufficiently emphasised in recent years to render the treatment of soil with boron compounds a matter of practical agricultural interest. The action of borax and boric acid on dry rot or heart rot in sugar beet figures prominently in this connection. Whether boron deficiency is the direct cause of the disease or is a contributory factor increasing susceptibility to external attack, is still debated in some quarters. The present trend is towards the view that heart rot is a boron-deficiency disease and not a microbial infection.[85] G. Wimmer and H. Ludecke [86] indicate that soil applications of boric acid may improve crop yields and sugar returns without decreasing liability to dry rot. The incidence of the disease is decreased by any condition which retards leaf growth. Assimilation of boron by plants appears to be heavily restricted by soil alkalinity,[87] and it is in these conditions that heart rot is particularly severe.[88] Boron is also shown to stimulate the germination of pollen grains,[89] to correct the toxic action of heavy metals, *e.g.*, of excessive amounts of iron,[90] and in some cases to influence the level of nitrogen intake by plants.[91]

The action of zinc in preventing or correcting certain diseased conditions in plants has been noted in a number of papers, *e.g.*, in correcting " bronzing " in tung trees [92] and " white bud " in maize.[93]

[83] *Soil Sci.*, 1934, **37**, 79; *B.*, 1934, 373.

[84] O. S. Orth, G. C. Wickwire, and W. E. Burge, *Science*, 1934, **79**, 33; *A.*, 1934, 334.

[85] W. Hughes and P. A. Murphy, *Nature*, 1935, **135**, 395; *B.*, 374.

[86] *Z. Ver. deut. Zucker-Ind.*, 1934, **84**, 627; *B.*, 1935, 38.

[87] G. A. Talibi, *Z. Pflanz. Düng.*, 1935, **39**, 257; *B.*, 867; M. A. Belousov, *Arb. Chem. Sektors U.S.S.R.*, **2**, 20; *B.*, 690.

[88] E. Foex and H. Burgevin, *Compt. rend. Acad. Agric. France*, 1934, **20**, 978; *B.*, 1935, 472.

[89] T. Schmucker, *Planta*, 1934, **23**, 264; *A.*, 1935, 552.

[90] W. E. Loomis and J. J. Wilson, *Proc. Iowa Acad. Sci.*, 1933, **40**, 53; *B.*, 1935, 1011.

[91] F. Terlikowski and K. Milkowski, *Rocz. Nauk. roln. leśn.*, 1934, **31**, 167; *B.*, 1935, 967.

[92] H. Mowry and A. F. Camp, *Florida Agric. Exp. Sta. Bull.*, 1934, No. 273; *B.*, 1935, 603.

[93] R. M. Barnette and J. D. Warner, *Soil Sci.*, 1935, **39**, 145; *B.*, 742.

J. Dufrenoy and H. S. Reed [94] conclude that zinc and iron have a specific effect on assimilation processes. This may be related to the observation of T. Thunberg [95] that zinc (and also cadmium) influences oxidation–reduction processes in plant materials.

Biochemistry of Moulds.

In the period elapsing since the last reference to this subject in these Reports a very considerable amount of research has been recorded. Although no spectacular achievements have appeared, the steady advance in our knowledge of the nutrition and metabolism of the moulds necessitates notice here.

Mineral Nutrition.—The intake of bases by *A. niger* is examined by E. Rennerfelt,[96] who shows that the course of intake of minerals depends not only on the permeability of the tissues and on the actual and relative concentrations of the different ions in the substrate, but also on the capacity of the cells to accumulate individual ions. Under normal conditions spores contain larger amounts of cations than does the mycelium. The ease of intake is in the general order $K^{\cdot} > Mg^{\cdot\cdot} > Na^{\cdot}$. Antagonistic effects are shown by both calcium and magnesium in respect of potassium. According to E. I. Sotnikov,[97] magnesium appears to have a specific effect in increasing the growth and citric acid production of *A. niger*, but this effect is observed only when the base is supplied as nitrate. Rossi,[98] on the other hand, regards magnesium supplied as sulphate as having a favourable influence on, without being essential to, the growth of the mould. In another paper,[99] the same author records magnesium sulphate in certain media as actually causing a decrease in dry matter production. Certain moulds appear to be highly sensitive to injury by magnesium, and it is notable that in a number of such cases the addition of calcium salts to the nutrient counteracts magnesium toxicity.[1] Strontium can, at least in part, replace calcium in this effect, which is attributed to the influence of the bases on colloidal phenomena in the tissue. Apart from its nutrient function, calcium can also influence the growth of *A. niger* by activating the utilisation of carbohydrates in potassium-deficient media.[2] C. Pontillon [3] also shows that potassium may be partially replaced by sodium or magnesium in its physiological activity within the fungal system. The ill effects of inadequate supplies of potassium on the carbohydrate metabolism of *A. niger* are accompanied by an accumulation of ammonia in the mycelium and the appearance of considerable amounts of oxalic acid in the substrate.[4]

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[94] *Ann. agron.*, 1934, **4**, 637; *A.*, 1935, 266.

[95] *Skand. Arch. Physiol.*, 1934, **69**, 247; *A.*, 1935, 1038.

[96] *Planta*, 1934, **22**, 221; *A.*, 1934, 1139.

[97] *Compt. rend. Acad. Sci. U.S.S.R.*, 1934, **3**, 273, 279; *A.*, 1934, 1263.

[98] G. Rossi and G. Scandellari, *Biochim. Terap. sperim.*, **19**, 92; *A.*, 1934, 1405.

[99] *Idem, Atti Congr. naz. Chim.*, 1933, **4**, 795; *A.*, 1934, 1263.

[1] U. Stoess, *Diss.*, Göttingen, 1932; *A.*, 1935, 535.

[2] C. Pontillon, *Compt. rend. Soc. Biol.*, 1934, **117**, 647; *A.*, 1935, 255.

[3] *Ibid.*, 1935, **119**, 349; *A.*, 1027.

The effects of the so-called "secondary" nutrients continue to receive attention. The essential character of zinc for the growth of *A. niger*, recognised for some years, is further investigated by G. Lohmann,[5] who makes quantitative measurements of relationships between dry matter yields and the concentration of zinc in the nutrient. Zinc-growth curves thus obtained have much in common with those for nitrogen and phosphate. The toxicity of relatively high concentrations of zinc is dependent partly on the actual concentration and partly on the nature and relative proportions of other substances in the medium. The action of zinc on the growth of the fungus is paralleled by that on the invertase activity, although the optimum zinc concentrations for the two functions are not the same. The maximum accumulation of citric and gluconic acids by *A. niger* is associated with specific concentrations of zinc sulphate, which vary somewhat according to the particular strain used. It is shown that zinc influences the respiratory activity of the organism and its ability to utilise sugar.[6] Observations of V. S. Butkevitsch and S. A. Barinova [7] show that in the large-scale manufacture of citric acid by *A. niger* yields are increased by additions of zinc salts to media used for inoculation cultures, but not by direct admixture with the sugar mash.

The influence of iron and other nutrients on acid production by moulds is considered in the section dealing with acids. Extensive consideration of the requirements of *A. niger* in respect of iron, zinc, copper, and manganese is given by R. A. Steinberg,[8] and K. Pirschle [9] presents a systematic examination of the effects of a wide range of nutrient and other inorganic acids and bases on the growth and sporulation of this organism.

Nitrogen Nutrition of Moulds.—Many recent investigations of the influence of various sources of nitrogen on the growth and metabolism of moulds deal with comparisons of nitrates and ammonium salts for this purpose, and the close relationship between carbon and nitrogen metabolism is frequently emphasised. For instance, H. Härdtl [10] shows that during the most active growth period of *A. niger*, the steady increase in the absolute nitrogen content of the culture is accompanied by a decline in the percentage of nitrogen, the relative changes being dependent on the proportions of carbon and nitrogen supplied. Increasing amounts of sugar in the nutrient accelerate growth and intensify respiratory activity. Appreciable formation of citric acid, however, occurs only with low levels of supply of nitrogen. As a result, in high-nitrogen cultures, acid production is delayed until the nitrogen source has been largely utilised. The composition of cultures of several species of *Aspergillus* on ammonium- and nitrate-media is recorded by S. Yamagata.[11] Usually the carbon and hydrogen contents vary but little, but that of nitrogen is markedly influenced by the nature of the source of nitrogen and by the relative proportions of carbon and nitrogen in the nutrient, a low C : N ratio being associated with high nitrogen content in the culture. Ammonium-nutrients lead to higher proportions of nitrogen in the organism than do nitrate-nutrients, irrespective of the source of carbon. The respiratory quotient of *A. oryzæ* varies with the nature of the nitrogen supply in the order, nitrate $>$ nitrite $>$ ammonium salts, the order being preserved with all the carbon sources examined. D. Bach and D. Desbordes [12] record that in acid glucose media *A. repens* reduces nitrates quantitatively to ammonia, which appears in the substrate, no increase in dry matter production taking place. This action reaches a maximum at p_H 4·4—5·0. In more alkaline media ($p_H > 6{\cdot}6$) nitrate reduction is still high, but exosmosis of ammonia ceases and growth proceeds normally. The initial stage of the utilisation of nitrites by a number of mould species appears to be the production of ammonia (but never of nitrate) even in neutral or alkaline media.[13] Relationships between carbon and nitrogen metabolism and the reaction of the medium, in the case of *Fusarium lycopersici* and *F. lini*, are examined by G. Luz.[14] With ammonium nitrate as source of nitrogen, the first stage of growth in media having p_H 3·9 is marked by the production of organic acids and a corresponding decrease in p_H. Subsequently there is a period of preferential intake of nitrate and a steady increase in p_H to 7·5. At this point, utilisation of ammonia becomes dominant. With the exhaustion of the sugar supply, ethyl alcohol and organic acids produced in the earlier stages become the sources of carbon and the medium becomes increasingly alkaline. The stages at which changes of carbon and nitrogen sources take place are identical. The exhaustion of sugar also coincides with a definite change in the ash content of the mycelium.

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[4] A. Rippel, *Arch. Mikrobiol.*, 1934, **5**, 561; *A.*, 1935, 535.

[5] *Ibid.*, p. 31; *A.*, 1934, 697.

[6] G. Vassiliev, *Biochem. Z.*, 1935, **278**, 226; *A.*, 1027.

[7] *Schr. zentr. biochem. Forschungsinst. Nahr. Genussm., Moscow*, 1932, **2**, 163; *B.*, 1934, 118.

[8] *Bull. Torrey Bot. Club*, 1935, **62**, 81; *A.*, 1166.

[9] *Planta*, 1934, **23** 177; *A.*, 1935, 535.

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[10] *Biochem. Z.*, 1934, **268**, 104; *A.*, 1934, 452.

[11] *Acta Phytochim.*, 1934, **8**, 107, 117; *A.*, 1934, 1262.

[12] *Compt. rend.*, 1933, **197**, 1463, 1772; *A.*, 1934, 112, 220.

[13] K. Sakaguchi and W. Y. Chang, *J. Agric. Chem. Soc. Japan*, 1934, **10**, 459; *A.*, 1934, 1405.

[14] *Phytopath. Z.*, 1934, **7**, 585; *A.*, 1935, 535.

The production of urea from peptone by various species of *Aspergillus* and *Penicillium* is also influenced by the source of carbon available. T. Chrzaszcz and M. Zakomorny[15] show that, in general, small concentrations of glucose favour the accumulation of urea, but larger amounts have the reverse effect and favour the production of citric and oxalic acids. Ethyl alcohol and acetic acid invariably lower the yield of urea. It is probable that guanidine is an intermediate product in this degradation process. The two changes guanidine ⟶ urea, and urea ⟶ ammonia are entirely separate functions and the effects of the various carbonaceous materials represent the resultant of their separate actions on the individual stages. The observations of T. Miwa and S. Yoshii[16] have a bearing on this point. *A. niger* and *P. glaucum* are found to produce urease as well as urea on ammonium nitrate media, or from protein hydrolysates, the formation of the enzyme being favoured by the presence of glucose. In media containing large amounts of ammonium nitrate, M. Lemoigne and R. Desveaux[17] record the production of hydroxylamine by *A. niger*.

Production of Organic Acids by Moulds.—The mechanism of the formation of citric acid by moulds is still a matter of controversy. V. S. Butkevitsch and colleagues[18] reject the view that sugars are converted into citric acid through the intermediate formation of acetic acid.[19] Citric acid formed in sodium acetate media is said to be derived from mycelium and not directly from the acetate, and the increased production of acid resulting from larger additions of acetate to the medium is ascribed to the strong inhibitory action of acetate on the utilisation of citric acid by the mould. The formation of citric acid and the utilisation of acetates by fungi are two distinct processes. The source of oxalic acid may be mycelium, the sugar, or the sodium acetate. In another publication[20] it is contended that oxalic acid is formed in the mycelium by fission of sugars without the intermediate production of formic acid. This is contrary to the views of T. Chrzaszcz and M. Zakomorny,[21] who postulate the decomposition of formic acid into oxalic acid and carbon dioxide. This theory is supported by observations of K. Bernhauer and F. Slanina [22] that *A. niger* gives 60% yields of oxalic acid from sodium formate in dilute solutions. At higher concentrations of the formate there is considerable degradation to carbon dioxide and water and the yield of oxalic acid is much lowered. High yields (60—77%) of oxalic acid are also obtained from acetic, succinic, fumaric, glycollic, aconitic, and citric acids.

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[15] *Biochem. Z.*, 1934, **273**, 31; **275**, 97; *A.*, 1934, 1263; 1935, 254.

[16] *Sci. Rep. Tokyo Bunrika Daigaku*, 1934, **1**, 243; *A.*, 1934, 928.

[17] *Compt. rend.*, 1935, **201**, 239; *A.*, 1166.

[18] With E. V. Menzschinskaja and E. I. Trofimova, *Biochem. Z.*, 1934, **272**, 290, 364; *A.*, 1934, 1139, 1263.

[19] *Ann. Reports*, 1932, **29**, 272.

[20] V. S. Butkevitsch, *Biochem. Z.*, 1934, **272**, 371; *A.*, 1934, 1263.

In a later paper Butkevitsch [23] explores another aspect of this problem by examining acid production by *A. niger* in relation to mineral nutrition. The accumulation of citric acid is associated with a deficiency of phosphorus and sulphur or of nitrogen. Yields of gluconic and oxalic acids are also lowered by inadequate supplies of phosphorus or nitrogen or magnesium, but are increased by lack of sulphur. Deficiency of potassium intensifies the production of oxalic and, to a less extent, of gluconic acids, whereas simultaneous shortage of potassium and magnesium causes the almost complete disappearance of citric acid. M. Giordani [24] records that the accumulation of citric acid by *A. niger* is lowered by the presence of iron salts, which tend to accelerate its oxidation to oxalic acid and carbon dioxide. This effect and also the inhibiting action of nitrogen compounds on citric acid production are said to be corrected by addition to the medium of a sodium citrate buffer.[25] The retarding influence of iron salts on the production of gluconic acid by several species of *Penicillium* is recorded by A. Angeletti and colleagues,[26] who show that, if the amount of iron present is small, the ultimate yield of gluconic acid, though delayed, may become even higher than that in iron-free media.

According to R. Bonnet and R. Jacquot [27] the amount of oxalic acid produced by *A. niger* increases with the age of the culture when nitrogen is supplied as potassium nitrate, but none is formed when ammonium salts are used. In nitrate-cultures the acid occurs as an unutilisable by-product in amounts regulated by the energy balance of the culture. Citric acid is formed in spores, is translocated to mycelium during growth, and subsequently reappears in the substrate during the autolysis of old cultures.

[21] *Biochem. Z.*, 1935, **279**, 64; *A.*, 1166.

[22] *Ibid.*, 1934, **274**, 97; *A.*, 1935, 124.

[23] With A. G. Timofeeva, *ibid.*, 1935, **275**, 405; *A.*, 406.

[24] *Chimica e l'Ind.*, 1935, **17**, 77; *A.*, 662.

[25] V. Bolcato, *Giorn. Chim. ind. appl.*, 1934, **16**, 552; *A.*, 1935, 255.

[26] With L. Merlo, *Ann. Chim. appl.*, 1934, **24**, 468; *A.*, 1934, 1405; with D. Ponte, *ibid.*, 1935, **25**, 217; *A.*, 1166.

[27] *Compt. rend.*, 1935, **200**, 1968; *A.*, 1027.

The respiratory exchange of *A. niger* is investigated by S. Michael.[28] In glucose media with excess of calcium carbonate, the $CO_2 : O_2$ ratio is maintained approximately at unity. In the early stages of growth a very small proportion of the sugar is used for purely respiratory purposes, the majority being oxidised to gluconic acid. Under these conditions the carbon dioxide output is derived mainly from the carbonate. In older cultures in which citric and oxalic acids are being formed, the respired carbon dioxide forms an increasing proportion of the total. In non-neutralised media the period of active formation of acid is marked by a considerable decrease in the respiratory quotient, which, however, again approaches unity at a later stage. Gluconic acid production is shown by E. Kardo-Syssojeva [29] to be favoured by excess of calcium carbonate. Addition to the nitrogen supply results in still larger accumulations of the acid in acid media, but has an inhibitory action in the presence of calcium carbonate.

Fatty Products of Fungal Development.—Examination of the fat production of *Penicillium javanicum*,[30] amounting at times to 40% of the dry matter of the mycelium, shows this to reach its maximum at a period of about one-third of the full growth period (dry weight increase) of the culture. High-sugar media (30—40%) are necessary for optimum fat yields, whereas for optimum mycelial growth approximately 20% of sugar is required. The maximum fat yield is coincident, in point of time, with maximum titratable acidity in the substrate. G. E. Ward and G. S. Jamieson [31] obtain, by hydrolysis of the fat, palmitic, stearic, oleic, α- and β-linoleic, and *n*-tetracosoic acids. F. M. Strong and W. H. Peterson [32] find the same acids, though in different proportions, in *Aspergillus sydowi*, together with a phospholipin. The unsaponifiable fraction of the alcohol–ether extract consists of 66% of sterols, among which ergosterol is identified. The lipins of *Penicillium aurantiobrunneum* yield a similar series of compounds.[33]

The production of lipins by moulds varies considerably with the conditions of culture. For instance, various species of *Aspergillus* grown on glucose–malt media produce a higher proportion of lipins and less protein matter than when grown on glucose–mineral salt preparations.[34] In an examination of the production of lipins by *A. fischeri*, E. A. Prill, P. R. Wenck, and W. H. Peterson [35] show that different strains show variations in fat content, in the iodine value of the fats, and in the proportions of phospholipins and sterols produced. With individual strains, the following general effects are noted. With glucose–ammonium nitrate–mineral salt media an increase in glucose concentration is associated with a higher fat production, a decrease in sterols, and a lowering of the iodine value of the fatty acids. Similar effects on the two last-named factors also result from increases in the nitrogen supply. In the range p_H 2·0—8·0 the fat yield increases with alkalinity. Higher temperatures decrease fat production. Exhaustion of glucose from the medium is followed by a decrease in the percentage of fat and phospholipin, although the iodine value of the fat suffers no further change.

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[28] *Biochem. Z.*, 1934, **274**, 397; *A.*, 1935, 254.

[29] *Ibid.*, 1933, **266**, 337; *A.*, 1934, 112.

[30] L. B. Lockwood, G. E. Ward, O. E. May, H. T. Herrick, and H. T. O'Neill, *Zentr. Bakt. Par.*, 1934, II, **90**, 411; *A.*, 1935, 535; also G. E. Ward, L. B. Lockwood, O. E. May, and H. T. Herrick, *Ind. Eng. Chem.*, 1935, **27**, 318; *A.*, 662.

[31] *J. Amer. Chem. Soc.*, 1934, **56**, 973; *A.*, 1934, 697.

[32] *Ibid.*, p. 952; *A.*, 1934, 697.

[33] E. H. Kroeker, F. M. Strong, and W. H. Peterson, *ibid.*, 1935, **57**, 354; *A.*, 535.

New Substances isolated from Mould Cultures.—The outstanding work of Raistrick and co-workers requires far greater space for adequate review than is available here, but some brief reference must be made to certain of the new substances which have been isolated, characterised, and in a number of cases synthesised in his laboratory, following intensive examination of mould products. Among the metabolic products of *Penicillium Charlesii* were isolated *carolic*, $C_9H_{10}O_4$, *carolinic*, $C_9H_{10}O_6$, *carlic*, $C_{10}H_{10}O_6$, and *carlosic*, $C_{10}H_{12}O_6$, acids. Structurally, these acids are found to be related to ascorbic acid and show similarities in absorption spectra.[36] *Penicillium minio-luteum* grown on a glucose medium yields miniolutcic acid, identified as the γ-lactone of $\alpha\beta$-dihydroxy-$\beta\gamma$-dicarboxy-*n*-tetradecoic acid.[37] Three pigments are isolated from the *Aspergillus glaucus* series, *viz.*, flavoglaucin, $C_{19}H_{28}O_3$, auroglaucin, $C_{19}H_{22}O_3$, and rubroglaucin, $C_{16}H_{12}O_5$.[38] These pigments are apparently specific to the series and serve also to subdivide the series into three groups according to their distribution. A yellow pigment, fulvic acid,[39] $C_{14}H_{12}O_8$, occurs in *Penicillium griseofulvum*, *P. flexuosum*, and *P. brefeldianum* when grown on a glucose–

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[34] L. M. Pruess, E. C. Eichinger, and W. H. Peterson, *Zentr. Bakt. Par.*, 1934, II, **89**, 370; *A.*, 1934, 810.

[35] *Biochem. J.*, 1935, **29**, 21; *A.*, 255.

[36] P. W. Clutterbuck, W. N. Haworth, H. Raistrick, G. Smith, and M. Stacey, *Biochem. J.*, 1934, **28**, 94; *A.*, 1934, 452; P. W. Clutterbuck, H. Raistrick, and F. Reuter, *ibid.*, 1935, **29**, 300, 871, 1300; *A.*, 327, 662, 898.

[37] J. H. Birkinshaw and H. Raistrick, *ibid.*, 1934, **28**, 828; *A.*, 1934, 927.

[38] B. S. Gould and H. Raistrick, *ibid.*, p. 1640; *A.*, 1934, 1263.

[39] A. E. Oxford, H. Raistrick, and P. Simonart, *ibid.*, 1935, **29**, 1102; *A.*, 786.

ammonium tartrate–mineral salt substrate. Certain strains of *Aspergillus terreus* produce terrein, $C_8H_{10}O_3$, from glucose under conditions in which other strains yield only succinic and oxalic acids.[40]

E. Nishikawa records the isolation of mellein, $C_{10}H_{10}O_3$ [identified as the lactone of 6-α (or β)-hydroxypropylsalicylic acid], from *Aspergillus melleus*.[41] Oosporin, $C_{10}H_4O_2$, and aurantin are isolated from *Oospora aurantin*.[42]

Algæ.

The output of research work relating to the biochemistry of algæ maintains a steady level, although, perhaps of necessity, it is of a somewhat scattered character. Nevertheless it is of interest to separate a brief record of recent work in this field from the rather overwhelming volume of publications in general plant biochemistry. General relationships between light intensity and the distribution, colour, and carbon assimilation of algæ form the subject of extensive investigations by C. Montfort,[43] in the case of green, brown, and red algæ, and by A. Seybold [44] in the case of submerged marine species. R. Lami [45] examines the distribution of marine types from sea-shore pools in relation to the reaction of the aqueous substrate and to lighting. The reaction of the water immediately surrounding the algæ is characteristic of the species, provided there is adequate exposure to light, but, with insufficient illumination, becomes dependent on the actual light intensity. F. E. Meier,[46] working with unicellular green algæ, shows that in many cases some chlorophyll is produced even in darkness, and that best growth is obtained with intermittent illumination. Within certain limits, an increase in light intensity causes a proportionate increase in the number of cells produced. *Stichiococcus bacillaris* produces good growth in red and infra-red lights. Chlorophyll formation in *Chlorella vulgaris* and other species is examined by G. Polacci.[47] In iron-free media, chlorophyll continues to be produced and growth is maintained if magnesium pyrrole-2-carboxylate is supplied. If magnesium is supplied in the alternative form of sulphate,

[40] H. Raistrick and G. Smith, *Biochem. J.*, 1935, **29**, 606; *A.*, 662.

[41] *J. Agric. Chem. Soc. Japan*, 1933, **9**, 772, 1059; *A.*, 1934, 562, 810.

[42] H. Nishikawa, *Proc. Imp. Acad. Tokyo*, 1934, **10**, 414; *A.*, 1934, 1139.

[43] *Jahrb. wiss. Bot.*, 1934, **79**, 493; *A.*, 1934, 1273.

[44] *Ibid.*, p. 593; *A.*, 1934, 1274.

[45] *Compt. rend.*, 1934, **199**, 615; *A.*, 1934, 1274.

[46] *Smithsonian Miscell. Coll.*, 1934, **92**, No. 5, 14 pp.; No. 6, 27 pp.; *A.*, 1934, 1418.

[47] *Ber. deut. bot. Ges.*, 1935, **53**, 540; *A.*, 1039.

new growth obtained has a high leucoplast but no chloroplast contents. The latter reappears when the pyrrole compound is again added. The theory is thus confirmed that the function of iron in relation to chlorophyll production is that of a catalyst in the formation of the pyrrole derivative. Temperature variations affect the respiration rate and carbon assimilation of algæ in different ways.[48] In *Stichococcus bacillaris*, parallel effects on the two functions are induced. In *Oocystis*, the same occurs at temperatures up to 22°, above which respiration increases the more rapidly. On the other hand, temperature affects the respiration of *Chlamydomonas* more strongly than the assimilation rate only at the lower ranges of temperature.

Several papers deal with the distribution of cellulose and associated compounds. In a number of red and brown algæ G. L. Naylor and B. Russell-Wells [49] record 2—15% of cellulose. The separation of cellulose from *Laminaria digitata* by T. Dillon and T. Otuama [50] yielded samples giving only glucose on complete hydrolysis. In seaweeds examined by P. Klason [51] there occurred 60% of cellulose, 30% of lignin, and smaller proportions of methyl pentoses. The lignin is characterised by having no methoxy-groups and by possessing a hydroxyl instead of an aldehydo-group. The formula $NH_2{\cdot}C_6H_3(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ is suggested. The proportion of xylose : hexose is 1 : 1, as compared with 3 : 2 in the higher plants. Following up earlier work, H. Colin and E. Guéguen[52] have established the presence of floridoside in many varieties of *Florideæ*.

In an investigation of the metabolism of calcareous algæ, P. Haas and T. G. Hill [53] demonstrate the presence, in aqueous extracts of *Corallina officinalis*, of hexa-acetylfloridoside and a polypeptide of aspartic acid. Relationships between seasonal variations of the floridoside and amino-nitrogen contents indicate that the formation of peptides is attributable to a lack of balance between the carbon and the nitrogen metabolism. Seasonal variations are also traced in the ratio of $CaCO_3 : MgCO_3$ in the incrustations of *C. squamata*.[54]

The presence of sterols in certain algæ is noted by E. Montignie.[55]

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[48] F. van der Paauw, *Planta*, 1934, **22**, 396; *A.*, 1935, 549.

[49] *Ann. Bot.*, 1934, **48**, 635; *A.*, 1934, 1146.

[50] *Sci. Proc. Roy. Dublin Soc.*, 1935, **21**, 147; *A.*, 550.

[51] *Svensk Kem. Tidskr.*, 1935, **47**, 215; *A.*, 1434.

[52] *Compt. rend.*, 1933, **197**, 1688; *A.*, 1934, 121.

[53] *Biochem. J.*, 1933, **27**, 1801; *A.*, 1934, 121.

[54] P. Haas, T. G. Hill, and W. K. H. Karstens, *Ann. Bot.*, 1935, **49**, 609; *A.*, 1178.

[55] *Bull. Soc. chim.*, 1935, [v], **2**, 194; *A.*, 673.

Heilbron and colleagues,[56] in a detailed examination of *Fucus vesiculosus*, have isolated and characterised a new sterol, fucosterol, $C_{29}H_{48}O$, which also occurs in *Felvetia canaliculata* and, together with sitosterol, in *Nitella opaca*. It is regarded as the characteristic algal sterol. In a further paper,[57] *F. vesiculosus* is shown to contain fucoxanthin (probably a dihydroxycapsorubin) but no xanthophyll, and from the dead tissue, β-carotene and zeaxanthin are isolated. Lutein, taraxanthin, and hentriacontane occur in several species examined. From *Nitella opaca* and *Oedogonium* is obtained a phytosterolin, $C_{35}H_{66}O_6$. The algal lipins appear to be characteristic for each species and related to their habitat.

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[56] I. M. Heilbron, R. F. Phipers, and H. R. Wright, *J.*, 1934, 1572; *A.*, 1934, 1347.

[57] I. M. Heilbron, E. G. Parry, and R. F. Phipers, *Biochem. J.*, 1935, **29**, 1369, 1376, 1382; *A.*, 1040.

ANALYTICAL CHEMISTRY.

During the period covered by this Report more than 1500 abstracts of papers concerned with analysis have appeared in *British Chemical Abstracts*, and it will at once be evident that no attempt to cover the whole field could be made. Physical methods of analysis, which have formed the subject of special monographs in the last two Reports, have been omitted, and other subjects such as colorimetry and mineral analysis must be left to a later Report. It has been considered advisable in this year's survey, however, to devote a special section to water analysis, which was last dealt with as a separate subject in the Annual Report for 1926.

INORGANIC ANALYSIS.

Quantitative.

Storage of Weights.—A subject of interest and concern to all engaged in accurate quantitative work, especially in view of the increasing use of methods dealing with amounts of material on the micro- and the semi-micro-scale, is the change in mass which weights may undergo during their storage and use. In a timely research, J. J. Manley [1] has investigated the nature, origin, and masses of the films which frequently appear on weights. The most pronounced films are acquired by gilded weights, and chromium-plated ones suffer the least change. The exceptional density of these films and their corroding powers have been traced to the acid character of the glue which is used in lining the boxes, and, occasionally, to the imperfect washing of the dyed velvet itself. In view of these findings, a simple method of storing has been worked out, in which these difficulties are overcome by using charcoal to absorb and retain any gases which may be developed, and by which the constancy in mass of precision weights is ensured.[2]

Conrady System of Weighing.—In 1922, A. E. Conrady [3] described a method of weighing which gives an accuracy of 0·001 mg. with a load of 100 g., using an analytical balance of robust design with only slight structural modifications. The underlying principle aims at eliminating, by a process of cancellation, the errors involved in an ordinary double weighing. W. H. J. Vernon[4] again directs attention to this method by describing in detail its application to routine work. The method appears to deserve more general consideration than it has received, and should be of service in determinations of a semi-micro nature, or even in work on a micro-scale where the expense and disadvantages of a micro-balance have to be avoided.

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[1] *Phil. Mag.*, 1933, [vii], **16**, 489; *A.*, 1933, 927.

[2] *Idem, ibid.*, 1935, [vii], **19**, 243; *A.*, 467.

[3] *Proc. Roy. Soc.*, 1922, [*A*], **101**, 211; see *Ann. Reports*, 1930, **27**, 208.

Standards for Volumetric Analysis.—During the period under review, attention has been devoted to volumetric standards (see also *Ann. Reports*, 1934, **31**, 295). Cyanogen bromide, which can readily be obtained and preserved in a condition of analytical purity, has been applied to the standardisation of acids, sodium thiosulphate, and silver nitrate.[5] Adipic,[6] salicylic,[7] and ψ-cumenesulphonic[8] acids have each in turn been recommended as acidimetric standards. R. H. Curtis[9] standardises hydrochloric acid against Iceland spar, precipitates the calcium chloride formed as oxalate, and uses this to standardise potassium permanganate, thus obtaining a direct link to oxidation–reduction determinations. J. W. Young[10] also describes a method for hydrochloric acid using calcite.

In this connexion it is indeed surprising that the constant boiling-point method for the preparation of a standard solution of this acid[11] is not more widely used. This excellent method is quick, exact, and compares well with other accepted methods,[12] and it gives good results even in inexperienced hands.

Sodium carbonate suitable for standardisation purposes is prepared[13] by heating sodium hydrogen carbonate at 156—280°, or at the boiling point of nitrobenzene for 100 minutes. J. Lindner and N. Figala[14] prefer to heat it to constant weight at 300°, and state that the hydrochloric acid required for a given amount of sodium carbonate is, on the average, 0·006% less than the theoretical. A new variation of normal procedure is introduced by L. Waldbauer, D. C. McCann, and L. F. Tuleen,[15] who wash the anhydrous carbonate with alcohol and dry it at 110°. They find that it does not decompose below 450°, a temperature well above that required for the preparation from the acid carbonate, but E. Preston and W. E. S. Turner [16] obtain a slight decomposition, apparently due to atmospheric moisture, on heating for a day in air at 400°. They recommend that the pure carbonate for analytical purposes be heated not above this temperature.

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[4] *Chem. and Ind.*, 1934, **53**, 211; *A.*, 1934, 384.

[5] M. Møller, *Z. anal. Chem.*, 1934, **99**, 351; *A.*, 1935, 183.

[6] A. H. Meyling, *J. S. African Chem. Inst.*, 1935, **18**, 23; *A.*, 462; F. T. van Voorst, *Chem. Weekblad*, 1928, **25**, 22; *A.*, 1928, 262; N. Schoorl, *ibid.*, p. 73; *A.*, 1928, 262.

[7] S. Škramovský, *Coll. Czech. Chem. Comm.*, 1933, **5**, 143; *A.*, 1933, 686.

[8] D. Tischtschenko, *J. Appl. Chem. Russia*, 1933, **6**, 1182; *A.*, 1934, 267.

[9] *Chem. and Ind.*, 1934, **53**, 135; *A.*, 1934, 380.

[10] *Canadian Chem. Met.*, 1934, **18**, 218; *A.*, 1935, 315.

[11] G. A. Hulett and W. D. Bonner, *J. Amer. Chem. Soc.*, 1909, **31**, 390; *A.*, 1909, ii, 342; W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," 1929, pp. 135, 142.

[12] G. W. Morey, *J. Amer. Chem. Soc.*, 1912, **34**, 1027; *A.*, 1912, ii, 986.

[13] J. Stalony-Dobrzański, *Rocz. Chem.*, 1934, **14**, 1106; *A.*, 1935, 315; see also Hillebrand and Lundell, *op. cit.*, p. 137.

[14] *Z. anal. Chem.*, 1933, **91**, 105; *A.*, 1933, 135.

The error introduced in acidimetry by the presence of carbonate in standard alkali, discussed at length by T. Miłobedzki and W. Szczypiński,[17] varies according to the conditions of addition of the alkali to the acid, and to the indicator used. They recommend the use of carbonate-free solutions prepared by Sørensen's method.

A. V. Filosofov [18] determines the titre of potassium permanganate solutions by means of calcium carbonate, and potassium ferrocyanide in the presence of sulphuric acid can conveniently be used for 0·01*N*-solutions with erioglaucin as indicator.[19] According to W. Wesly,[20] iron prepared from the pentacarbonyl is purer than piano wire and is as good as electrolytic iron for this standardisation.

In the past, much confidence has been placed in the standardisation of potassium permanganate by means of sodium oxalate, which is regarded in many quarters as one of the best fundamental volumetric processes available. Now, however, the usual method of titration [21] has been called in question. In a critical examination of the subject, R. M. Fowler and H. A. Bright [22] find that the slow addition of the permanganate to a hot solution of the oxalate in dilute sulphuric acid (2 : 98) leads to results which may be as much as 0·4% high when compared with other primary standards, and that in order to obtain satisfactory agreement with the values found with iron, arsenious oxide, or potassium dichromate, a modified procedure, which they detail, is necessary. In view of the importance of this standardisation, it is to be hoped that independent confirmation of this work will soon be made.

Potassium dichromate is standardised by treating arsenious acid with less than its equivalent of dichromate and finishing the titration with ceric sulphate or potassium permanganate, osmium tetroxide being used as catalyst and *o*-phenanthroline ferrous complex as indicator.[23]

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[15] *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 336; *A.*, 1934, 1188.

[16] *J. Soc. Glass Tech.*, 1934, **18**, 182T; *A.*, 1935, 48.

[17] *Rocz. Chem.*, 1934, **14**, 1088; *A.*, 1935, 315; see also W. W. Kay and H. L. Sheehan, *Biochem. J.*, 1934, **28**, 1795; *A.*, 1934, 1322.

[18] *J. Appl. Chem. Russia*, 1934, **7**, 1085; *A.*, 1935, 318.

[19] E. J. de Beer and A. M. Hjort, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 120; *A.*, 597.

[20] *Z. anal. Chem.*, 1933, **91**, 341; *A.*, 1933, 246.

[21] R. S. McBride, *J. Amer. Chem. Soc.*, 1912, **34**, 393; *A.*, 1912, ii, 494.

[22] *J. Res. Nat. Bur. Stand.*, 1935, **15**, 493.

The factors which affect the standardisation of sodium thiosulphate with potassium dichromate have been studied in detail by H. C. S. Snethlage.[24] Reproducible results can be obtained only in dilute solutions, and the accuracy of the determination is affected by illumination, concentration of acid, and rate of addition of potassium iodide. With sulphuric acid these factors are less important than when hydrochloric acid is used. Results accurate to 0·01% are claimed for the procedure finally recommended.

Limiting ratios of the weights of the reagents concerned in this standardisation are laid down by Z. Nakai,[25] and acidimetric and alkalimetric titrations of sodium thiosulphate are also described.[26]

The stability of aqueous solutions of this reagent and methods for their preservation still continue to be investigated. R. A. Kölliker [27] sterilises glassware and solutions by live steam and, by maintaining them under aseptic conditions, obtains a change in normality of only 0·1% during a period of 500 days, whilst F. J. Watson [28] preserves the titre almost indefinitely by buffering to p_H 9·0—9·5; with 0·01*M*-borax; 0·1*N*-solutions remained unchanged after 3 years. Solutions of this concentration are unaffected in titre by bubbling pure carbon dioxide or oxygen through them for 2—3 hours, according to I. Bellucci and I. Damiani,[29] who attribute a slow decrease in normality to decomposition by water, followed by oxidation by atmospheric oxygen. In dealing with the stability of certain volumetric solutions, E. P. Hedley [30] finds that 0·1*N*-sodium thiosulphate showed the same factor for approximately 3 months, but he prefers arsenious oxide solution, prepared according to Kolthoff's directions,[31] as a primary standard.

The purification of $K_2TiO(C_2O_4)_2,2H_2O$ for the preparation of iron-free solutions of titanium sulphates,[32] and that of pure titanium dioxide from the tetrachloride and its use in standardising ferric ammonium sulphate [33] are also described.

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[23] H. H. Willard and (Miss) P. Young, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 57; *A.*, 317.

[24] *Rec. trav. chim.*, 1934, **53**, 567; *A.*, 1934, 745.

[25] *Bull. Fishery Exp. Sta. Gov. Gen. Chosen*, 1933, *D*, No. 3, 1; *A.*, 1934, 619.

[26] A. Sconzo, *Ind. chim.*, 1933, **8**, 297; *A.*, 1933, 477.

[27] *Z. anal. Chem.*, 1932, **90**, 272; *A.*, 1933, 41.

[28] *J. Soc. Chem. Ind. Victoria*, 1932, **32**, 679; *A.*, 1933, 136.

[29] *Gazzetta*, 1934, **64**, 69; *A.*, 1934, 619.

[30] *Proc.* VI *Congr. S. Afr. Sugar Tech. Assoc.*, 1932, 6; *A.*, 1932, 1101.

[31] " Volumetric Analysis," II, 363.

There appears to be a need for a review of the whole subject of primary and secondary standards for volumetric analysis. A critical consideration of published methods by a group of experienced analysts should do much to clarify the whole position, and a selection by them of trustworthy methods and procedures would be invaluable to all engaged in accurate analytical work.

Indicators.—Indicators which have been recently investigated must receive brief mention. They include diphenylcarbazone, $Fe_3[Fe(CN)_6]_2$ containing an excess of $Fe(CN)_6'''$,[34] diamine-fast-bordeaux-6BS and diamine-fast-violet-BBN,[35] *o*-cresolphthalein [36] and dichlorofluorescein [37] as adsorption indicators for argentometric titrations, Victoria-blue-BX as an internal indicator in ceriometry,[38] and α-naphthaflavone for the titration of arsenic and antimony solutions with potassium bromate.[39] For the arsenic titration, Ponceau-3R, methylene-blue, Bordeaux-B, safranine, Azure-II, chrysoidine, and saffron-yellow are all said to be more suitable than methyl-orange.[40]

Among many organic compounds examined, phenyl-*p*- and -*m*-toluidine are satisfactory oxidation–reduction indicators for use with dichromate in the absence of mercury salts, and naphthidine and a product derived from the action of ethyl sulphate on acetyldiphenylamine can be used even in their presence.[41] The sodium salt of diphenylbenzidinesulphonic acid is also recommended as an indicator of this type.[42]

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[32] R. Roseman and W. M. Thornton, jun., *J. Amer. Chem. Soc.*, 1935, **57,** 328; *A.*, 460.

[33] W. W. Plechner and J. M. Jarmus, *Ind. Eng. Chem.* (*Anal.*), 1934, **6,** 447; *A.*, 1935, 56.

[34] E. Chirnoagă, *Z. anal. Chem.*, 1935, **101,** 31; *A.*, 719.

[35] E. A. Kocsis, *Z. anorg. Chem.*, 1935, **221,** 318; *A.*, 316.

[36] Y. Uzumasa and Y. Mikaye, *J. Chem. Soc. Japan*, 1934, **55,** 627; *A.*, 1935, 53.

[37] H. R. Fleck, R. F. G. Holness, and A. M. Ward, *Analyst*, 1935, **60,** 32; *A.*, 315; K. Bambach and T. H. Rider, *Ind. Eng. Chem.* (*Anal.*), 1935, **7,** 165; *A.*, 835.

[38] J. M. Caldwell and M. E. Weeks, *Trans. Kansas Acad. Sci.*, 1934, **37,** 117; *A.*, 1935, 1339.

[39] E. Schulek, *Z. anal. Chem.*, 1935, **102,** 111; *A.*, 1215; R. Uzel, *Coll. Czech. Chem. Comm.*, 1935, **7,** 380; *A.*, 1471.

[40] T. Sotgia-Rovelli, *Boll. chim.-farm.*, 1935, **74,** 265; *A.*, 718.

[41] L. E. Straka and R. E. Oesper, *Ind. Eng. Chem.* (*Anal.*), 1934, **6,** 465; *A.*, 1935, 56.

[42] L. A. Sarver and W. von Fischer, *ibid.*, 1935, **7,** 271; *A.*, 1092.

β-Methylumbelliferone provides a fluorescing indicator for the titration of coloured solutions,[43] and the magnesium compound of 8-hydroxyquinoline one for titrating acids with alkalis.[43a]

Benzoylauramine-G is described as a new indicator for Kjeldahl nitrogen determinations.[44]

The indicator properties of many dinitroanilineazonaphtholsulphonic acids are described by H. Wenker,[45] but none is as good an indicator as nitrazine-yellow [46] which, together with its 8-halogen derivatives, has been further investigated.[47]

Mixed indicators giving sharper end-points than their constituents alone are recommended by S. Hähnel and B. Holmberg,[48] and by H. A. J. Pieters,[49] who regards methyl-orange as the best indicator for carbonate titrations.

A study of the salt error of methyl-red, phenolphthalein, and bromothymol-blue in certain acid–base titrations [50] has been made, and a useful introduction to some of the applications of the more modern indicators has also been published [51] during the period under review.

Reagents.—In addition to the now well-known reagents, 8-hydroxyquinoline, dithizone, etc., the use of which is being steadily developed and extended, three others appear to be worthy of notice.

Thiolacet-β-naphthalide. This reagent, for convenience named "thionalide," forms complex derivatives with many metals, and its application in analysis has been surveyed by R. Berg and W. Roebling.[52] The metals can be determined directly by weighing the complex, by ignition, by titration with iodine, or colorimetrically and nephelometrically. The sensitivity of the reagent permits its use in micro- as well as in macro-determinations; for silver, this is such that silver ions can be detected in filtrates from precipitated silver chloride. In sodium hydroxide–cyanide solution, with or without tartrate, it is specific for thallium and is especially suitable for toxicological work.

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[43] A. G. Pukirev and M. S. Maslova, *Zavod. Lab.*, 1934, **3**, 1038; *A.*, 1935, 316.

[43a] H. R. Fleck, R. F. G. Holness, and A. M. Ward, *loc. cit.*, ref. (37).

[44] J. T. Scanlan and J. D. Reid, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 125; *A.*, 639.

[45] *Ibid.*, p. 40; *A.*, 315.

[46] *Idem*, *Ind. Eng. Chem.*, 1934, **26**, 350; *A.*, 1934, 500.

[47] E. S. Vasserman, *Zavod. Lab.*, 1934, **3**, 868; *A.*, 1935, 52.

[48] *Svensk Kem. Tidskr.*, 1935, **47**, 4; *A.*, 462.

[49] *Chem. Weekblad*, 1935, **32**, 539; *A.*, 1336.

[50] S. Kilpi and A. Laaksonen, *Soumen Kem.*, 1935, **8**, *B*, 9; *A.*, 594.

[51] A. D. Mitchell, *Institute of Chemistry*, 1934; *A.*, 1935, 182.

[52] *Ber.*, 1935, **68**, [*B*], 403; *A.*, 591; *Angew. Chem.*, 1935, **48**, 430, 597; *A.*, 950, 1338; R. Berg, *ibid.*, 1934, **47**, 404.

Thiolbenzthiazole. This is used for copper in presence of cadmium, the metals of Group IIIb, alkaline earths, and alkalis, but other metals of Group II, as well as silver and thallium, are quantitatively precipitated.[53] It also serves for macro- and micro-determinations of cadmium when other metals, except copper, are absent.[54]

Phosphomolybdic acid. J. W. Illingworth and J. A. Santos[55] revive interest in the possibilities of this acid as an analytical reagent. As a precipitant for cæsium or potassium, it is more sensitive than either chloroplatinic acid or sodium cobaltinitrite, and its application to the determination of potassium is being investigated.

Gravimetric and Volumetric Methods for the Determination of the Elements.—The papers published on this subject during the period under review are as numerous as ever and the task of making a suitable selection has not been easy. Many doubtless excellent methods will receive no mention. The choice has been based partly on the personal appeal of a method, but mainly, it is hoped, on its possible utility. Before they replace well-tried and satisfactory procedures, new methods must establish a claim to one or more definite advantages, such as greater ease of manipulation and speed of execution, a more favourable conversion factor, and, most important of all, a cleaner separation from accompanying ions. It is not sufficient that they should be merely new. Methods which are applicable only to pure solutions of a metal would appear to be of little value, for, in practice, it is the separation from other ions which is of chief importance and constitutes the main difficulty in effecting an accurate analysis. Furthermore, although all new methods of determination and detection are welcome and have their possible uses, it is unfortunate that so many of them apply to elements for which satisfactory methods already exist, whilst for elements such as tin, calcium, or potassium, for example, for which separations are scarce or leave much to be desired, little seems to be forthcoming.

Group I. Small amounts of silver in the presence of lead, zinc, gold, bismuth, etc., can be determined titrimetrically or colorimetrically with dithizone,[56] which has also been applied in the determination of traces (0·0005—0·02%) of thallium in the presence of other metals.[57]

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[53] G. Spacu and M. Kuraš, *Z. anal. Chem.*, 1935, **102**, 24; *A.*, 1094.

[54] *Idem, ibid.*, p. 108; *A.*, 1216.

[55] *Nature*, 1934, **134**, 971; *A.*, 1935, 185.

[56] H. Fischer, G. Leopoldi, and H. von Uslar, *Z. anal. Chem.*, 1935, **101**, 1; *A.*, 719.

[57] L. A. Haddock, *Analyst*, 1935, **60**, 394; *A.*, 950.

Group II. Elimination of interference by bismuth has been effected in the dithizone method for lead,[58] which is sensitive to approx. 0·001 mg. of lead in metals [59] and in biological material.[60] H. H. Willard and J. J. Thompson [61] separate this metal from copper, cadmium, nickel, zinc, etc., by precipitation as $Pb_3H_4(IO_6)_2$, which can be either weighed or determined volumetrically. Lead can also be precipitated as $Pb(C_7H_6O_2N)_2$ by anthranilic acid [62] and similarly determined. The conditions for precipitation of the chromate in forensic analysis have been studied,[63] but the method cannot be used in presence of large amounts of other metals.[64]

Volumetric methods [65] and a nephelometric micro-method [66] for mercury are described.

An investigation of the behaviour of material containing copper on fusion with sodium carbonate and sulphur shows that the copper dissolved in an aqueous extract of the melt increases with the proportion of sulphur used and is augmented by the presence of tin; a quantitative separation of the copper from such material is not possible.[67] This is in harmony with the observation that the known solubility of cupric sulphide in alkaline polysulphides increases rapidly with the sulphur content of the latter, its concentration, and temperature. In sodium monosulphide, the cupric sulphide is practically insoluble.[68] Further work has been carried out [69] on the separation of copper by means of salicylaldoxime and dimercaptothiodiazole,[70] whilst *p*-homosalicylaldoxime is recommended [71] for the detection and determination of both copper and nickel. Quinaldinic acid also is used for the micro-determination of the former by a method which separates it from lead, manganese, nickel, phosphate, etc., if suitable precautions are taken in washing.[72] In the usual iodometric method for copper, the addition of a soluble thiocyanate near the end-point is claimed [73] to increase its sharpness and accuracy, whilst the adsorption of starch iodide by the precipitated cuprous salt is said to be reduced by the addition of a solution of white shellac in alcohol.[74]

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[58] C. E. Willoughby, E. S. Wilkins, jun., and E. O. Kraemer, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 285; *A.*, 1094.

[59] E. S. Wilkins, jun., C. E. Willoughby, E. O. Kraemer, and F. L. Smith, *ibid.*, p. 33; *A.*, 531.

[60] *Idem*, *ibid.*; O. B. Winter, H. M. Robinson, F. W. Lamb, and E. J. Miller, *ibid.*, p. 265; *A.*, 1094.

[61] *Ibid.*, 1934, **6**, 425; *A.*, 1935, 55.

[62] H. Funk and F. Römer, *ibid.*, 1935, **101**, 85; *A.*, 720.

[63] K. Höll, *ibid.*, 1935, **102**, 4; *A.*, 1182.

[64] A. W. Middleton, *J. Ind. Hygiene*, 1935, **17**, 7; *A.*, 317.

[65] S. Škramovský and R. Uzel, *Časopis czechoslov. Lék.*, 1934, **14**, 33; *A.*, 1934, 1323; G. Denigès, *Bull. Soc. Pharm. Bordeaux*, 1934, **72**, 5; *A.*, 1935, 186; M. Schtschigol, *J. Appl. Chem. Russia*, 1935, **8**, 160; *A.*, 950.

[66] S. I. Ssinjakova, *Z. anal. Chem.*, 1935, **100**, 190; *A.*, 464.

[67] R. Höltje and W. Kahmen, *Z. anorg. Chem.*, 1935, **223**, 234; *A.*, 1088.

[68] R. Höltje and J. Beckert, *ibid.*, 1935, **222**, 240; *A.*, 576.

[69] M. Ishibashi and H. Kishi, *J. Chem. Soc. Japan*, 1934, **55**, 1060, 1065, 1067; *A.*, 1935, 720.

[70] P. Rây and J. Gupta, *J. Indian Chem. Soc.*, 1935, **12**, 308; *A.*, 1094; J. Gupta, *ibid.*, 1934, **11**, 403; *A.*, 1934, 982.

[71] C. H. Kao and K. H. Chen, *J. Chinese Chem. Soc.*, 1935, **3**, 22; *A.*, 720.

Of all methods for the determination of an element, those of Marsh and Gutzeit must, in the past, have received as much attention as, if not more than, any other single method, and fresh contributions have again been made during the year. In describing modified apparatus and technique for the Marsh–Liebig method, G. Lockemann [75] points out that the customary hard-glass Kjeldahl flask may yield small amounts of arsenic, and recommends silica flasks in their stead. W. Deckert,[76] however, states that this dissolution of arsenic is appreciable only on the first occasion such a flask is used, but Lockemann maintains his objection.[77] Further, when mercury is present, satisfactory arsenic mirrors are said to be unobtainable.[78] Other modifications of the Marsh [79] and the Gutzeit [80] method have also been detailed.

Methods for tin which do not depend on its reducing power are still all too few, and a much-needed organic reagent which will do for the determination of quadrivalent tin what the oximes have done for that of nickel, still awaits discovery.

In alkali molybdates, molybdenum is determined as the silver salt,[81] and it can be precipitated as the 8-hydroxyquinoline derivative, $MoO_2(C_9H_6ON)_2$, without disturbance due to the presence of a phosphate.[82]

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[72] P. R. Rây and J. Gupta, *Mikrochem.*, 1935, **17**, 14; *A.*, 318.

[73] H. W. Foote and J. E. Vance, *J. Amer. Chem. Soc.*, 1935, **57**, 845; *A.*, 837.

[74] J. R. Caldwell, *ibid.*, p. 96; *A.*, 318; cf. A. D. Mitchell and A. M. Ward, "Modern Methods in Quantitative Chemical Analysis," 1932, p. 67.

[75] *Angew. Chem.*, 1935, **48**, 199; *A.*, 596; *Z. anal. Chem.*, 1935, **100**, 20; *A.*, 554.

[76] *Ibid.*, **101**, 338; *A.*, 948.

[77] *Ibid.*, p. 340; *A.*, 948.

[78] H. Kühl and B. Czyżewsky, *Pharm. Zentr.*, 1934, **75**, 660; *A.*, 1934, 1322.

[79] J. Gangl, *Oesterr. Chem.-Ztg.*, 1935, **38**, 64; *A.*, 718.

[80] L. W. Strock, *Z. anal. Chem.*, 1934, **99**, 321; *A.*, 1935, 184; J. D. Gnessin, *Pharm. Zentr.*, 1934, **75**, 719; *A.*, 1935, 53; cf. also R. Steinbrück, *ibid.*, 1935, **76**, 5; *A.*, 184; C. J. Snijders, jun., and A. J. W. van der Drift, *Chem. Weekblad*, 1935, **32**, 275; *A.*, 718.

[81] L. W. McCay, *J. Amer. Chem. Soc.*, 1934, **56**, 2548; *A.*, 1935, 187.

[82] S. Ishimaru, *J. Chem. Soc. Japan*, 1934, **55**, 732; *A.*, 1935, 56.

With material containing elementary sulphur and selenium, sodium thiosulphate and thioselenate are formed by boiling with 10% aqueous sodium sulphite, after which the selenium is precipitated by warming with formaldehyde.[83] According to V. Hovorka,[84] selenious acid is quantitatively reduced to selenium by acetone saturated with sulphur dioxide. This author has also studied in detail the reduction by hydrazine and finds that a direct separation of selenium from cadmium, lead, vanadium, tungsten, etc., by this means is possible only under certain conditions.[85]

Pyridine precipitates tellurium from its tetrachloride as the dioxide, which is weighed after drying at 120°.[86]

The micro-determination of platinum, iridium, and associated potassium and chlorine,[87] and the volumetric determination of rhenium with ferric sulphate, potassium dichromate and permanganate, or ceric sulphate, according to the nature of the compound present,[88] are also described.

Group III. In the third analytical group the use of 8-hydroxyquinoline has been further applied to thorium,[89] which is precipitated as $Th(C_9H_6ON)_4,C_9H_7ON$,[90] and to zirconium,[91] after precipitation as $Zr(C_9H_6ON)_4$, which can be weighed directly, titrated with bromate, or ignited to ZrO_2. According to other workers,[92] however, the last compound and its bromine derivative are unsuitable for the accurate determination of zirconium. The reagent has also been used to separate metals of this group from phosphate ions, which can then be determined in the usual way.[93] In an important paper, H. B. Knowles [94] gives the conditions necessary for the successful separation of aluminium and beryllium from many metals, using 8-hydroxyquinoline, and discusses the reasons for the somewhat high results which the method gives. A procedure for determining aluminium in alloys which may contain iron, nickel, molybdenum, etc., has also been described.[95] Finally, the bluish-black precipitate, $(C_9H_6ON)_4V_2O_3$, which is obtained with 8-hydroxyquinoline and a vanadate in presence of acetic acid, has been utilised for the gravimetric determination of vanadium.[96]

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[83] E. Cheraskova and L. Veissbruth, *Z. anal. Chem.*, 1935, **102**, 353; *A.*, 1336.

[84] *Chem. Listy*, 1935, **29**, 73; *A.*, 718.

[85] *Coll. Czech. Chem. Comm.*, 1935, **7**, 182; *A.*, 948.

[86] A. Jílek and J. Koťa, *ibid.*, 1934, **6**, 398; *A.*, 1934, 1322.

[87] H. D. K. Drew, H. J. Tress, and G. H. Wyatt, *J.*, 1934, 1787; *A.*, 1935, 56.

[88] W. Geilmann and W. Wrigge, *Z. anorg. Chem.*, 1935, **222**, 56; *A.*, 464.

[89] F. Hecht and W. Ehrmann, *Z. anal. Chem.*, 1935, **100**, 98; *A.*, 464.

[90] Cf. F. J. Frere, *J. Amer. Chem. Soc.*, 1933, **55**, 4362; *A.*, 1934, 82.

[91] G. Balanescu, *Z. anal. Chem.*, 1935, **101**, 101; *A.*, 721.

[92] P. Süe and G. Wétroff, *Bull. Soc. chim.*, 1935, [v], **2**, 1002; *A.*, 989.

[93] S. Ishimaru, *J. Chem. Soc. Japan*, 1935, **56**, 62; *A.*, 1337; see also ref. 82.

[94] *J. Res. Nat. Bur. Stand.*, 1935, **15**, 87; *A.*, 1216.

Vanadous ammonium sulphate, $VSO_4,(NH_4)_2SO_4,6H_2O$, which is more stable in air than VSO_4, is another reagent which has been applied to this group in volumetric methods for ferric iron and chromium as chromate.[97] The conditions under which cupferron may be used to determine copper, ferrous and ferric iron,[98] and also micro-quantities of aluminium in plant material by a nephelometric method,[99] have been investigated.

The B.P. (1932) method for determining metallic iron in the presence of iron oxides is stated [1] to give results which are inaccurate and variable, and a modification of Wilner's method [2] is preferred. Micro-methods for iron consist of reduction of a hydrochloric acid solution by passage through a silver sponge reductor, followed by titration with 0·002—0·015*N*-ceric sulphate, using $\alpha\alpha'$-dipyridyl as indicator,[3] or reduction with electrolytic cadmium (zinc being less trustworthy in a micro-reductor), followed by titration with 0·005*N*-permanganate using cyanin-B or erioglaucin-A as indicator.[4] Pyridine, according to P. Spacu,[5] will separate iron completely as $Fe(OH)_3$ from solutions containing ferric iron and cobalt, which can then be determined as $[Co(C_5H_5N)_4(CNS)_2]$ in the remaining solution.

Contrary to all accepted procedure [6] are the findings [7] that zirconium should be precipitated in sulphuric acid which is not more concentrated than 1%, and that titanium must first be eliminated in the phosphate method for the determination of small quantities of zirconium in rocks. This latter element is also determined by means of *n*-propylarsonic acid,[8] whilst thorium is determined on both macro- and micro-scales by means of picrolonic acid.[9]

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[95] T. Heczko, *Chem.-Ztg.*, 1934, **58**, 1032; *A.*, 1935, 187.

[96] R. Montequi and M. Gallego, *Anal. Fis. Quim.*, 1934, **32**, 134; *A.*, 1935, 464.

[97] P. C. Banerjee, *J. Indian Chem. Soc.*, 1935, **12**, 198; *A.*, 838.

[98] E. Benedetti, *Rev. Fac. Cienc. quim., La Plata*, 1934, **9**, 59; *A.*, 1935, 720.

[99] P. Meunier, *Compt. rend.*, 1934, **199**, 1250; *A.*, 1935, 186.

[1] F. Hartley, W. H. Linnell, F. E. Read, and H. G. Rolfe, *Quart. J. Pharm.*, 1935, **8**, 100; *A.*, 720.

[2] E. Merck, *Z. anal. Chem.*, 1902, **41**, 710.

[3] C. J. van Nieuwenburg and (Miss) H. B. Blumendal, *Mikrochem.*, 1935, **18**, 39; *A.*, 1095.

[4] J. Knop and O. Kubelková, *Z. anal. Chem.*, 1935, **100**, 161; *A.*, 464.

[5] *Compt. rend.*, 1935, **200**, 1595; *A.*, 838.

[6] See W. F. Hillebrand "The Analysis of Silicate and Carbonate Rocks," U.S. Geol. Survey, 1929, Bull. No. 700, p. 173; W. F. Hillebrand and G. E. F. Lundell, *op. cit.*, p. 446.

[7] V. A. Oschman and T. K. Zertschaninova, *Redk. Met.*, 1934, **3**, No. 6, 36; *A.*, 1935, 1339.

The precipitation of aluminium alone from a mixture containing aluminium, manganese, nickel, and cobalt by hexamethylenetetramine [10] revives interest [11] in the possibilities of a more extended use of this reagent which appears to possess certain advantages. Volumetric methods for aluminium,[12] beryllium,[13] chromium (micro),[14] as well as a gravimetric method for beryllium,[15] have also been put forward. The solubility of strongly-ignited chromium sesquioxide in warm, dilute solutions of potassium bromate, whereby chromate is formed, is an unexpected reaction which is of interest.[16]

After reduction to the quadrivalent state, vanadium is precipitated by ammonium benzoate as $VO(OBz)_2$ which can be ignited to the pentoxide; iron and chromium should be absent, but magnesium, aluminium, titanium, and some other metals are said not to interfere.[17] Alternatively, the precipitate of $[Co(NH_3)_6]_4(V_6O_{17})_3$, formed in acid solution with VO_3' and $Co(NH_3)_6^{\cdots}$, can be used for the quantitative separation of vanadium from iron, phosphate, arsenate, etc., but not from tungstate, molybdate, or lead.[18] For the volumetric determination of vanadium, A. J. Berry [19] applies the iodine cyanide method to the oxidation of V^{II} to V^{III}.

W. R. Schoeller and his co-workers make further contributions to the analytical chemistry of tantalum and niobium in dealing with the separation of the rare earths from the earth acids [20] and tungsten from titanium, niobium, tantalum, and zirconium.[21]

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[8] F. W. Arnold, jun., and G. C. Chandlee, *J. Amer. Chem. Soc.*, 1935, **57**, 8; *A.*, 319; G. C. Chandlee, *ibid.*, p. 591; *A.*, 598.

[9] F. Hecht and W. Ehrmann, *Z. anal. Chem.*, 1935, **100**, 87; *A.*, 464.

[10] T. Kôzu, *J. Chem. Soc. Japan*, 1935, **56**, 22; *A.*, 1338.

[11] Cf. C. Kollo and N. Georgian, *Bul. Soc. Chim. România*, 1924, **6**, 111; *A.*, 1925, ii, 330; P. Rây and A. K. Chattopadhya, *Z. anorg. Chem.*, 1928, **169**, 99; *A.*, 1928, 387; V. F. Stefanovski, *J. Appl. Chem. Russia*, 1934, **7**, 1288; *A.*, 1935, 318.

[12] M. K. Bachmutova, *Legk. Metal.*, 1934, **3**, No. 9, 37; *A.*, 1935, 1338.

[13] B. S. Evans, *Analyst*, 1935, **60**, 291; *A.*, 837.

[14] D. Brard, *Ann. Chim. analyt.*, 1935, [iii], **17**, 201, 257; *A.*, 1095, 1339.

[15] I. Iitaka, Y. Aoki, and T. Yamanobe, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1935, **14**, 741; *A.*, 1216.

[16] R. Lydén, *Z. anorg. Chem.*, 1935, **223**, 28; *A.*, 834.

[17] F. M. Schemjakin, *Zavod. Lab.*, 1934, **3**, 986; *A.*, 1935, 319; F. M. Schemjakin and V. F. Tschapigin, *J. Appl. Chem. Russia*, 1935, **8**, 536; *A.*, 1095.

[18] W. G. Parks and H. J. Prebluda, *J. Amer. Chem. Soc.*, 1935, **57**, 1676; *A.*, 1339.

[19] *Analyst*, 1934, **59**, 736; *A.*, 1935, 56.

[20] W. R. Schoeller and E. F. Waterhouse, *ibid.*, 1935, **60**, 284; *A.*, 838.

[21] A. R. Powell, W. R. Schoeller, and C. Jahn, *ibid.*, p. 506; *A.*, 1217.

J. A. Tschernichov and M. P. Karssajevskaja [22] find that, contrary to previous statements, niobium cannot be accurately determined by reduction with zinc amalgam and re-oxidation with standard ferric chloride.

α-Nitro-β-naphthol in acetic acid solution precipitates cobalt as $Co(C_{10}H_6ONO_2)_3$,[23] and in a suitable concentration of acid a quantitative separation from aluminium, chromium, nickel, and zinc can be obtained. If iron is first removed with zinc oxide, the method can be applied to cobalt steels.[24] In the well-known α-nitroso-β-naphthol method, C. H. Damon [25] advises the replacement of ammonium chloride and hydrochloric acid by sodium sulphate and acetic acid, respectively. A. Taurinš [26] determines this metal as a new complex, $[Co(NH_3)_6][HgI_3]_2$, by precipitation in an atmosphere of carbon dioxide with K_2HgI_4 from strongly ammoniacal solution, but the oxidation of the precipitate in air may restrict the popularity of the method.

Quantitative separations of metallic sulphates such as those of cobalt from nickel, iron from titanium, aluminium, zinc, or manganese, etc., can, according to L. Wöhler and K. Flick,[27] be effected by selective dissociation in a current of sulphur trioxide or the dioxide and oxygen at suitable temperatures, and the method has been used for the quantitative isolation of aluminium, iron, and titanium from bauxite.

A volumetric method involving precipitation of cobalt with ammonium thiocyanate and pyridine and titration of the excess CNS′ ion by silver nitrate appears to have been put forward more or less simultaneously by two independent groups of investigators.[28]

The solubility of nickel dimethylglyoxime [29] in hot solutions still seems to be disregarded. That this source of error is a real one can easily be checked, *e.g.*, in a nickel steel analysis a milligram or so of the nickel compound will always separate out on cooling a solution which has been filtered hot and washed with hot instead of cold water. The interference to which this method is subject in presence of large amounts of copper can be overcome by the addition of sodium hyposulphite prior to that of the oxime, and the method is then said to be particularly applicable to the analysis of nickel–copper alloys.[30] For those who prefer a volumetric ending to a determination, there is now available, in addition to the titration of the acid liberated by the reaction between nickel and dimethylglyoxime,[31] another method,[32] which determines, by means of ferric sulphate and permanganate, the hydroxylamine liberated when the nickel dimethylglyoxime is hydrolysed by boiling with dilute sulphuric acid. This method also is applicable to the determination of nickel in steels and coinage alloys when tartaric acid is present. The compound of copper with salicylaldoxime can be treated in a similar way.

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[22] *Z. anal. Chem.*, 1934, **99**, 398; *A.*, 1935, 721; cf. V. Schwarz, *Angew. Chem.*, 1934, **47**, 228; *A.*, 1934, 622.

[23] H. Herfeld and O. Gerngross, *Z. anal. Chem.*, 1933, **94**, 7; *A.*, 1933, 1025.

[24] C. Mayr, *ibid.*, 1934, **98**, 402; *A.*, 1934, 1324.

[25] *J. Chem. Educ.*, 1935, **12**, 193; *A.*, 1072.

[26] *Z. anal. Chem.*, 1935, **101**, 357; *A.*, 951.

[27] *Ber.*, 1934, **67**, [*B*], 1679; *A.*, 1934, 1320.

[28] J. T. Dobbins and J. P. Sanders, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 459; *A.*, 1935, 56; G. Spacu and M. Kuraš, *Bul. Soc. Ştiinţe Cluj*, 1934, **7**, 377; *A.*, 1934, 1323.

[29] P. Nuka, *Z. anal. Chem.*, 1933, **91**, 29; *A.*, 1933, 138.

Zinc in the presence of various metals is determined on both macro- [33] and micro-scales [34] by means of quinaldinic acid, whilst, according to C. Cimeran and P. Wenger,[35] the method of H. Funk and M. Ditt,[36] which uses anthranilic acid, is also suitable for microchemical work. A point of interest in connexion with the standard phosphate method for zinc is that decomposition of zinc ammonium phosphate to the pyrophosphate begins at 350° and is complete in 90 minutes at 520°.[37]

Group IV. The determination of the alkaline earths as oxalates continues to receive attention, and the behaviour of these oxalates, alone and together, when precipitated and washed by J. Dick's method,[38] has been further investigated.[39] For calcium, titration of the oxalate ion is preferable to weighing, but for barium, owing to the incompleteness of precipitation, and strontium the method appears to be unsatisfactory. Magnesium, which is thrown down as the dihydrate, is likely to be co-precipitated with the calcium, so a double precipitation is necessary in this case. Barium and strontium, when present, also interfere with the determination of calcium. H. Sibelius [40] considers that the determination of calcium as CaC_2O_4,H_2O following O. Brunck's directions [41] is trustworthy.

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[30] J. Ranedo, *Anal. Fis. Quim.*, 1934, **32**, 611; *A.*, 1935, 951.

[31] J. Holluta, *Monatsh.*, 1919, **40**, 281; *A.*, 1920, ii, 57.

[32] B. Tougarinoff, *Ann. Soc. Sci. Bruxelles*, 1934, **54**, [*B*], 314; *A.*, 1935, 187.

[33] P. Rây and A. K. Majundar, *Z. anal. Chem.*, 1935, **100**, 324; *A.*, 597.

[34] P. R. Rây and M. K. Bose, *Mikrochem.*, 1935, **17**, 11; **18**, 89; *A.*, 318, 1094.

[35] *Ibid.*, p. 53; *A.*, 1094.

[36] *Z. anal. Chem.*, 1933, **91**, 332; *A.*, 1933, 244.

[37] Z. H. Pan and C. H. Chiang, *J. Chinese Chem. Soc.*, 1935, **3**, 118; *A.*, 1093.

[38] *Z. anal. Chem.*, 1929, **77**, 352; *A.*, 1929, 901.

[39] J. Haslam, *Analyst*, 1935, **60**, 668; *A.*, 1338.

[40] *Suomen Kem.*, 1935, **8**, [*A*], 25; *A.*, 596.

[41] *Z. anal. Chem.*, 1933, **94**, 81; *A.*, 1933, 1024.

According to A. Ievinš,[42] ignition of calcium carbonate or oxalate over a gas flame yields an oxide containing SO_4'', and electric heating should therefore be employed.

Although no data are recorded, N. A. Tananaev[43] states that calcium and magnesium can be quantitatively extracted from barium and strontium by treatment of the dry nitrates with glacial acetic acid. If this be true, then this acid could with obvious advantage replace the fuming nitric acid which is used in S. G. Rawson's method[44] for the separation of calcium and strontium.

A volumetric micro-method for calcium[45] consists in the titration of excess picrolonate against methylene-blue in presence of chloroform, after removal of the metal by means of a standard solution of lithium picrolonate.

Group V. The determination of magnesium as $MgNH_4PO_4,6H_2O$, often used on the micro-scale, gives, on the macro-scale, results which compare favourably with those obtained by the pyrophosphate method.[46] The 8-hydroxyquinoline method has been further studied,[47] and volumetric determinations include a method for the precipitation of the magnesium as $MgNH_4AsO_4$ and then titration of the arsenious oxide after reduction with sulphur dioxide.[48]

No finality has yet been reached in the cobaltinitrite method for potassium. Each year sees its quota of papers on this subject. Different investigators seem able to evolve a method which satisfies their particular requirements, but no agreement on a standard procedure which will cover a wide range of concentration and conditions has been attained. The main difficulty still lies in achieving constancy of composition of the precipitate produced. H. W. Lohse[49] states that this varies between $KNa_2[Co(NO_2)_6]$ and $K_2Na[Co(NO_2)_6]$ according to conditions of precipitation, whilst C. S. Piper,[50] in an examination of modifications necessary to ensure quantitative recovery over the range 0·1—50 mg. K_2O, finds that the ratio of potassium to sodium in the precipitate varies according to the composition of solution and precipitant and to the conditions of precipitation. Error may also be introduced by the presence of ammonium salts in some brands of cobalt nitrate of reagent quality.[51] Other workers [52] describe modified methods. C. Peng [53] introduces a variation in the volumetric ending by decomposing the cobaltinitrite (equivalent to < 20 mg. K_2O) with dilute hydrochloric acid containing urea and titrating the excess of acid with alkali, whilst (Miss) H. Bennett and H. F. Harwood [54] improve it by utilising a cerimetric method.[54] Finally, A. Bolliger [55] precipitates the potassium (0·04—10 mg.) as picrate and titrates this with a standard methylene-blue solution.[56]

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[42] *Latvij. Univ. Rakstí*, 1935, **2**, 465; *A.*, 1338.

[43] *Z. anal. Chem.*, 1935, **100**, 391; *A.*, 719.

[44] *J. Soc. Chem. Ind.*, 1897, **16**, 113; *A.*, 1898, ii, 190; cf. W. Noll, *Z. anorg. Chem.*, 1931, **199**, 193; *A.*, 1931, 1259.

[45] A. Bolliger, *Austral. J. Exp. Biol.*, 1935, **13**, 75; *A.*, 1093.

[46] J. P. Mehlig, *J. Chem. Educ.*, 1935, **12**, 288; *A.*, 1093; see F. P. Treadwell and W. T. Hall, *op. cit.*, 1935, p. 81.

[47] M. Javillier and J. Lavollay, *Bull. Soc. Chim. biol.*, 1934, **16**, 1531; *A.*, 1935, 186; D. C. Vucetich, *Rev. Fac. Cienc. quím., La Plata*, 1934, **9**, 81; *A.*, 1935, 719; G. Creuss-Callaghan, *Biochem. J.*, 1935, **29**, 1081; *A.*, 837.

[48] W. Daubner, *Angew. Chem.*, 1935, **48**, 551; *A.*, 1216.

[49] *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 272; *A.*, 1093.

[50] *J. Soc. Chem. Ind.*, 1934, **53**, 392T; *A.*, 1935, 317.

The determination of sodium as sodium magnesium uranyl acetate after removal of potassium, as perchlorate, and other interfering ions has also been described.[57]

R. W. Feldmann [58] finds that the bismuth iodide method of N. A. Tananaev and E. P. Harmasch [59] gives inaccurate results for the determination of cæsium both in pure solutions of its salts and in mixtures with rubidium.

Anions. A mercurimetric method for the halogens, including fluorine, is described in detail, and a precision equal to that of the classical methods is claimed for it.[60] For fluorine in small amount, B. Visintin's procedure [61] is adversely criticised.[62] In the Volhard method for chloride, the addition of nitrobenzene eliminates the necessity of removing the precipitated silver chloride.[63] Three methods for the analysis of chlorides in the presence of thiocyanates have also been examined.[64] Volumetric micro-methods for chloride,[65] bromide in the presence of a large excess of chloride,[66] and bromide and iodide in the presence of chloride [67] have been put forward, and the precautions necessary for accurate work with 0·01N-iodine solutions have been defined.[68] The loss of iodine by volatilisation from dilute iodine–potassium iodide solutions during the passage of air has been investigated by W. A. Hough and J. B. Ficklen,[69] and a method for the determination of small quantities of iodides is described by M. L. Jean,[70] who applies it also to silver and chromate.

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[51] *J. Soc. Chem. Ind.*, 1935, **54,** 157T; *A.*, 836.

[52] S. D. Sunawala and K. R. Krishnaswami, *J. Indian Inst. Sci.*, 1934, **17,** [*A*], 105; *A.*, 1935, 54; K. Nowak, *Przemysł Chem.*, 1934, **18,** 509; *A.*, 1935, 185.

[53] *Trans. Sci. Soc. China*, 1934, **8,** No. 2, 153; *Proc. Internat. Soc. Soil Sci.*, 1935, **10,** 105; *B.*, 966.

[54] *Analyst*, 1935, **60,** 677; *A.*, 1337.

[55] *J. Biol. Chem.*, 1934, **107,** 229; *A.*, 1934, 1322.

[56] *J. Proc. Roy. Soc. N.S.W.*, 1933, **67,** 240; *A.*, 1934, 1017.

[57] F. Kögler, *Angew. Chem.*, 1935, **48,** 561; *A.*, 1215.

[58] *Z. anal. Chem.*, 1935, **102,** 102; *A.*, 1215.

[59] *Ibid.*, 1932, **89,** 256; *A.*, 1932, 1010.

[60] A. Ionescu-Matiu and S. Herscovici, *Bull. Soc. chim.*, 1934, [v], **1,** 1379; *A.*, 1935, 183.

[61] *Ann. Chim. appl.*, 1934, **24,** 315; *A.*, 1934, 980.

[62] M. Giordani, *ibid.*, p. 496; *A.*, 1935, 53.

[63] J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem.* (*Anal.*), 1935, **7,** 38; *A.*, 316.

[64] E. Cohen and K. Piepenbroek, *Z. anal. Chem.*, 1934, **99,** 258; *A.*, 1935, 183.

The best conditions for determining ClO_4' in the presence of various interfering ions have also been studied in detail,[71] and M. L. Nichols [72] discusses the reduction of chlorates and perchlorates by titanous chloride.

Cyanates can be titrated with silver nitrate using fluorescein as adsorption indicator.[73]

A review of methods used in the volumetric determination of sulphates [74] has been made, as well as a study of the reactions which occur in the precipitation of $Ba^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, or SO_4'' ions as barium or lead sulphates.[75] A method for the removal of carbon dioxide in micro-determinations of alkali carbonates is also described.[76]

In the determination of ferrocyanide by means of dichromate, a controlled acidity is essential; the application of the method to the determination of zinc is discussed.[77] Ferricyanide, potassium permanganate, and, indirectly, iron can be titrated on a micro-scale by means of 0·001N-solutions of indigo-carmine.[78]

Conditions for the complete precipitation of silica by ammonium molybdate have been studied; the silica in the precipitate can be determined gravimetrically, by titration with sodium hydroxide or by reduction and back-titration with permanganate.[79]

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[65] B. Bullock and P. L. Kirk, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 178; *A.*, 835.

[66] F. L. Hahn, *Mikrochem.*, 1935, **17**, 222; *A.*, 835.

[67] I. Bellucci, *Gazzetta*, 1934, **64**, 688; *A.*, 1934, 1321.

[68] J. Renaudin and (Mme.) Renaudin, *J. Pharm. Chim.*, 1934, [viii], **20**, 516; *A.*, 1935, 184.

[69] *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 460; *A.*, 1935, 52.

[70] *Bull. Soc. chim.*, 1935, [v], **2**, 605; *A.*, 717.

[71] C. Smeets, *Natuurwetensch. Tijds.*, 1934, **16**, 262; *A.*, 1935, 183.

[72] *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 39; *A.*, 316.

[73] R. Ripan-Tilici, *Z. anal. Chem.*, 1935, **102**, 32; *A.*, 1093.

[74] G. A. Ampt, *J. Proc. Austral. Chem. Inst.*, 1935, **2**, 10; *A.*, 462.

[75] Z. Karaoglanov and B. Sagortschev, *Z. anorg. Chem.*, 1935, **221**, 369; *A.*, 317.

[76] J. Mika, *Z. anal. Chem.*, 1935, **101**, 270; *A.*, 836.

[77] F. Burriel and F. Sierra, *Anal. Fis. Quim.*, 1934, **32**, 87; *A.*, 1935, 597.

[78] I. M. Korenman, *Mikrochem.*, 1935, **18**, 31; *A.*, 1095.

[79] S. Kitajima, *Bull. Chem. Soc. Japan*, 1935, **10**, 341; *A.*, 1337.

Various applications of titrations with alkaline permanganate, *e.g.*, PO_3''', CNS', IO_3', CN', etc., are described,[80] and those of Fajans's titration method are reviewed.[81]

Miscellaneous.—The p_H ranges for the precipitation of certain metals by anthranilic acid are recorded by H. Gotô,[82] and J. G. F. Druce [83] reviews the use of magnesium perchlorate (" anhydrone ") as a desiccant.[84]

Finally, in view of the steadily increasing use of perchloric acid in analytical work, the observation [85] that mixtures of aqueous solutions of this acid and organic substances are liable to explode, even in the cold, has its interest.

Qualitative.

General Methods for the Detection of Anions and Cations.—Although much attention has been focussed on the newer methods of detection of ions, the older, macro-methods have by no means been neglected, and an account of some of this work during the past year will now be given.

Numerous reactions, with their sensitivities, are recorded for thallium with a wide range of reagents,[86] and for the commoner members of the second analytical group, with potassium iodide and various aromatic and cyclic bases.[87] Tests for mercury depend on the formation of the complex ion HgI_4'',[88] followed by reduction with alkaline glycerol [89] or stannous chloride,[90] or of gold chloride.[91] The change in colour to blue, which the green flame due to copper undergoes in presence of carbon tetrachloride, serves to distinguish this element from other substances giving a green flame,[92] and in view of the use of α-benzoinoxime as a test for copper [93] the observation that nickel, platinum, and palladium form compounds with this reagent [94] is of interest. Cadmium can be precipitated by the addition of sodium selenide to the ammoniacal potassium cyanide solution in presence of copper, nickel, cobalt, or zinc, thus avoiding the doubt sometimes occasioned by the formation of rubianic acid in the usual group analysis. The test is sensitive to a few γ.[95] P. G. Popov [96] describes a test for this element in which it is claimed that other metals do not interfere. A modified procedure for the arsenic sub-group has been worked out,[97] and the colours produced by the reducing action of mercurous chloride have been used to detect and estimate small amounts of arsenic, gold, platinum, palladium, selenium, tellurium, and iodine.[98] In order to detect arsenic in presence of antimony, N. A. Tananaev and V. D. Ponomarjev [99] reduce its compounds to arsine by tin and hydrochloric acid, antimony yielding only the metal. Methods for the detection of small quantities of germanium in presence of arsenic,[1] the separation of the platinum metals by hydrogen under pressure,[2] and the detection of small amounts of indium, gallium, and thallium, using quinalizarin,[3] are also described.

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[80] H. Stamm, *Angew. Chem.*, 1934, **47**, 791; *A.*, 1935, 55.

[81] E. J. Kocsis and L. Pollák, *Acta Lit. Sci. Univ. Hung. Francisco-Joseph.*, 1934, **4**, 147; *A.*, 1935, 836; K. Fajans, in "Die chemische Analyse," vol. **33**, " Neure massanalytische Methoden," 1935, p. 161 *et seq.*

[82] *J. Chem. Soc. Japan*, 1934, **55**, 1156; *A.*, 1935, 720.

[83] *Chem. and Ind.*, 1935, **54**, 133; *A.*, 321.

[84] See also W. F. Hillebrand and G. E. F. Lundell, *op. cit.*, p. 45.

[85] J. R. Partington, *Chem. and Ind.*, 1935, **54**, 468; *A.*, 715.

[86] J. C. Munch and J. C. Ward, *J. Amer. Pharm. Assoc.*, 1935, **24**, 351; *A.*, 950.

[87] I. M. Korenman, *Z. anal. Chem.*, 1934, **99**, 402; *A.*, 1935, 720.

[88] P. I. Trischin, *J. Appl. Chem. Russia*, 1934, **7**, 1282; *Ukrain. Chem. J.*, 1934, **9**, 341; *A.*, 1935, 318, 950.

[89] M. Schtschigol, *J. Appl. Chem. Russia*, 1935, **8**, 158; *A.*, 950; *Khim. Farm. Prom.*, 1934, No. 1, 44; *A.*, 1934, 1323.

[90] N. A. Tananaev, *J. Appl. Chem. Russia*, 1935, **8**, 356; *A.*, 950.

[91] E. Stathis, *Z. anal. Chem.*, 1934, **99**, 106; *A.*, 1935, 55.

[92] P. Gabriel, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 420; *A.*, 1935, 55.

[93] Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 1935, p. 167.

Changes in the benzoate method for the separation of iron, aluminium, and chromium [4] make it applicable to qualitative analysis,[5] and a slight modification of the usual phosphate separation avoids coprecipitation of traces of zinc, cobalt, manganese, barium, and strontium.[6] Suitable methods for the inclusion of titanium and vanadium as an ordinary part of the third analytical group are indicated.[7]

The concentration of a precipitate at a liquid–liquid interface or in a non-miscible liquid is a device which is often of service in analysis, and it is now used [8] to separate nickel dimethylglyoxime from ferrous iron, and sulphur from certain sulphides, with *iso*-amyl alcohol.

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[94] J. S. Jennings, E. Sharratt, and W. Wardlaw, *J.*, 1935, 818; *A.*, 981.

[95] P. Krumholz and O. Kruh, *Mikrochem.*, 1935, **17**, 210; *A.*, 837.

[96] *Ukrain. Chem. J.*, 1934, **9**, 307; *A.*, 1935, 950.

[97] A. T. Lincoln and E. Olson, *J. Chem. Educ.*, 1935, **12**, 264; *A.*, 1092.

[98] G. G. Pierson, *Ind. Eng. Chem. (Anal.)*, 1934, **6**, 437; *A.*, 1935, 53.

[99] *Z. anal. Chem.*, 1935, **101**, 183; *A.*, 836.

[1] S. A. Coase, *Analyst*, 1934, **59**, 747; *A.*, 1935, 56.

[2] V. V. Ipatiev and V. G. Tronev, *Compt. rend. Acad. Sci. U.R.S.S.*, 1935, **2**, 29; *A.*, 951.

[3] E. Pietsch and W. Roman, *Z. anorg. Chem.*, 1934, **220**, 219; *A.*, 1934, 1323.

[4] I. M. Kolthoff *et al.*, *J. Amer. Chem. Soc.*, 1934, **56**, 812; *A.*, 1934, 621.

[5] L. Lehrman and J. Kramer, *ibid.*, p. 2648; *A.*, 187.

[6] E. Kahane, *Ann. Chim. analyt.*, 1935, [iii], **17**, 119; *A.*, 718.

[7] L. E. Porter, *Ind. Eng. Chem. (Anal.)*, 1934, **6**, 448; *A.*, 1935, 56; see also *idem*, *ibid.*, p. 138; *A.*, 1934, 502, concerning tungsten and molybdenum.

$Na_2[Hg(CNS)_4]$ is more sensitive than the corresponding potassium and ammonium compounds as a reagent for cobalt.[9]

Methods for the detection of calcium in presence of barium and strontium [10] and of potassium [11] are put forward. For the latter, zinc cobaltinitrite can replace the sodium salt when a test for sodium has subsequently to be made.[12] According to J. Červinka,[13] quinalizarin does not distinguish magnesium from barium, calcium, and strontium,[14] whilst zinc, aluminium, and ferric iron interfere with the development of the colour reaction.

A. P. Laurie [14a] deals with small particles of insoluble material by fusion with borax or microcosmic salt on a platinum wire and then applies tests for the metals directly by immersion of the bead in appropriate reagents.

A classification of anions is proposed by A. Hemmeler and M. Angelini,[15] who discuss also the difficulties arising from the presence of heavy metals. Among the new work on anions may be noted tests for fluoride ions,[16] halides in presence of thiocyanates,[17] bromide and a systematic analysis of mixtures of thiocyanate and halide ions,[18] traces of iodide in the presence of chlorates, bromates, and iodates ; [19] chlorate,[20] sulphurous acid,[21] thiosulphate,[22] nitrate,[23] nitrite,[24] cyanide,[25] ferricyanides in presence of ferrocyanides,[26] and chromates.[27]

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[8] A. M. Belousov and A. G. Belousova, *J. Appl. Chem. Russia*, 1934, **7**, 837; *A.*, 1935, 187.

[9] B. V. J. Cuvelier, *Z. anal. Chem.*, 1935, **101**, 108; *A.*, 721.

[10] N. A. Tananaev, *Ukrain. Chem. J.*, 1935, **10**, 15; *A.*, 949; *Z. anal. Chem.*, 1935, **100**, 391; *A.*, 719; E. R. Caley, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 445; *A.*, 1935, 54.

[11] B. Reichert, *Arch. Pharm.*, 1935, **273**, 232; *A.*, 596; C. N. Potschinok, *J. Appl. Chem. Russia*, 1935, **8**, 524; *A.*, 1093.

[12] J. Adams, M. Hall, and W. F. Bailey, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 310; *A.*, 1337.

[13] *Chem. Listy*, 1935, **29**, 35; *A.*, 1093.

[14] Cf. Feigl, *op. cit.*, p. 260.

[14a] *Analyst*, 1934, **59**, 746; *A.*, 1935, 55.

[15] *Ind. chim.*, 1934, **9**, 1343; *A.*, 1935, 317.

[16] L. Kulberg, *J. Gen. Chem. Russia*, 1934, **4**, 1440; *A.*, 1935, 717.

[17] G. B. Heisig and L. K. Heisig, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 249; *A.*, 1091.

[18] L. J. Curtman and H. Schneiderman, *Rec. trav. chim.*, 1935, **54**, 158; *A.*, 462.

[19] A. Vassiliou, *Praktika*, 1933, **8**, 324; *A.*, 1935, 52.

[20] H. R. Offord, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 93; *A.*, 594.

[21] H. Freytag, *Ber.*, 1934, **67**, [*B*], 1477; *A.*, 1934, 1321; *ibid.*, 1935, **68**, [*B*], 585; *A.*, 718.

[22] A. Blanck, *Z. anal. Chem.*, 1935, **101**, 194; *A.*, 836.

[23] P. G. Popov, *Ukrain. Chem. J.*, 1934, **9**, 310; *A.*, 1935, 948.

M. Eitel [28] has studied in some detail the colour reactions of nitrates and other oxidising agents with solutions of organic reagents, especially quinones, in concentrated sulphuric acid. Quinones not substituted in the nucleus give colour reactions with nitrate but not with nitrite, and *p*-benzoquinone is very suitable in this respect for solid substances. Diphenyleneglycine in concentrated sulphuric acid is, on the other hand, a sensitive reagent for nitrates in aqueous solutions.

Tests which involve inhibition of, or changes in, fluorescence are utilised for the detection of chlorine and bromine in air or gas mixtures,[29] of hyposulphites and sulphoxylates and "nascent" hydrogen,[30] and of nitrites.[31]

Drop Reactions.—A. "*Spot*" *Tests.* In view of the importance and increasing use of drop reactions, the so-called "spot" tests, the work done on them during the current period is again [32] summarised. These tests are finding many applications in mineralogy, petrology, and in both pure and applied chemistry, and when they are used with discrimination and due regard to possible interfering ions, they afford a valuable analytical weapon for attacking with ease problems which could be solved by macro-methods often only with difficulty and much uncertainty. Unfortunately, there is a tendency to regard some of these reactions as specific for a particular element when such is not the case. Too frequently, in fact, this claim has been based on a survey insufficiently comprehensive to justify it. These tests are particularly useful as confirmatory tests in an ordinary analysis *after* a group separation has been carried out, and they can deal very successfully with traces or small precipitates which so often are inclined to be troublesome in a qualitative analysis. In general, they are preferable to tests which depend on the formation and recognition of crystals under the microscope, in that they are quicker and easier to carry out, less susceptible to conditions, and much easier to interpret.

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[24] L. R. Catalano, *Riv. Min.*, 1931, **1**, 16; *A.*, 1935, 316; A. C. Bittencourt and A. Barreto, *Bol. Min. Agric.*, *Rio de Janeiro*, 1935, **23**, 7; *B.*, 225.

[25] L. J. Curtman and S. M. Edmonds, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 121; *A.*, 596.

[26] I. M. Korenman, *Z. anal. Chem.*, 1935, **101**, 417; *A.*, 1095.

[27] L. R. Catalano, *loc. cit.*, ref. (24).

[28] *Z. anal. Chem.*, 1934, **98**, 227; *A.*, 1934, 1322.

[29] H. Eichler, *Z. anal. Chem.*, 1934, **99**, 272; *A.*, 1935, 183.

[30] *Idem, ibid.*, p. 270; *A.*, 1935, 184.

[31] *Idem, ibid.*, 1935, **100**, 183; *A.*, 463.

[32] Cf. *Ann. Reports*, 1934, **31**, 314.

Tests for *bismuth* with thiocarbamides and other organic sulphur compounds are described and discussed.[33] *p*-Aminophenol hydrochloride is a sensitive reagent for *copper* and *iron*; other metals are said not to interfere.[34] *Copper* is also detected by the formation of the lilac-coloured compound $ZnHg(CNS)_4,CuHg(CNS)_4$.[35] In a critical study of the cacotheline test for *tin*,[36] attention is directed to the interferences which arise from the presence of many anions and cations: the test is by no means specific. The reddish-brown coloration obtained with As^{III} and 8-hydroxy-*N*-ethyltetrahydroquinoline hydrochloride (kairin) and ferric chloride can detect 6×10^{-10} g. of arsenic, but mercury, lead, and copper interfere.[37] A test for *antimony* in presence of a large excess of arsenic or tin is also described.[38] Whilst *osmium* reacts with thiourea only, *ruthenium* compounds react with this reagent and its *N*-alkyl or -aryl derivatives to give sensitive, blue to red, colorations,[39] which are suitable for drop reactions. A solution of strychnine in sulphuric acid is applied to the detection of *chromate* or *dichromate* ions[40] and of *manganese*.[41]

Indium can be detected by means of alizarin or quinalizarin and ammonia vapour, aluminium being suppressed by the addition of sodium fluoride, and zinc, nickel, cobalt, manganese, and iron being removed from the coloured spot with potassium cyanide.[42] The catechol test for *titanium*[43] is not specific, but its sensitiveness (1 in 5×10^6) makes it useful for identification after a separation has been effected.[44] E. Kahane[45] discusses G. Denigès's colour reaction between manganese and formaldoxime.[46] Naphthazarin is used for *magnesium*.[47] The alkali hypoiodite test for this metal is disturbed by ammonium, aluminium, and other cations.[48] Drop reactions for *cæsium* are few in number, but another test, sensitive to $0{\cdot}25 \times 10^{-6}$ g. of Cs per cu. mm., depends on the formation of the black compound $Cs_2Au_2PtBr_{12}$. Rubidium reacts only when present in certain concentrations, but the other alkali ions and ammonium do not interfere.[49]

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[33] J. V. Dubský, A. Okáč, and J. Trtílek, *Mikrochem.*, 1935, **17**, 332; *A.*, 1096; *Z. anal. Chem.*, 1935, **100**, 408; *A.*, 721; J. V. Dubský and A. Okáč, *Chem. Obzor*, 1934, **9**, 3; *A.*, 1934, 1324; P. Rây and J. Gupta, *J. Indian Chem. Soc.*, 1935, **12**, 308; *A.*, 1094.

[34] S. Augusti, *Mikrochem.*, 1935, **17**, 118; *A.*, 837.

[35] L. M. Kulberg, *J. Appl. Chem. Russia*, 1934, **7**, 1079; *A.*, 1935, 318.

[36] I. L. Newell, J. B. Ficklen, and L. S. Maxfield, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 26; *A.*, 319.

[37] W. Reppmann, *Z. anal. Chem.*, 1934, **99**, 180; *A.*, 1935, 184.

[38] G. Gutzeit, R. Weibel, and R. Duckert, *Arch. Sci. phys. nat.*, 1934, [v], **16**, Suppl., 62; *A.*, 1935, 464.

[39] B. Steiger, *Mikrochem.*, 1935, **16**, 193; *A.*, 332.

[40] S. Augusti, *ibid.*, 1935, **17**, 17; *A.*, 319.

[41] *Idem*, *Ann. Chim. appl.*, 1934, **24**, 535; *A.*, 1935, 55.

[42] A. S. Komarovski and N. S. Poluektov, *Mikrochem.*, 1935, **16**, 227; *A.*, 318.

[43] J. Piccard, *Ber.*, 1909, **42**, 4343; *A.*, 1910, i, 67; A. Rosenheim, B. Raibmann, and G. Schendel, *Z. anorg. Chem.*, 1931, **196**, 160; *A.*, 1931, 446.

[44] N. R. Pike, J. B. Ficklen, and I. L. Newell, *Ber.*, 1935, **68**, [*B*], 1023; *A.*, 951.

[45] *Ann. Chim. analyt.*, 1935, [iii], **17**, 175; *A.*, 951.

The application of these colour reactions to the detection of many elements in minerals is described by J. A. Watson,[50] and R. Jirkovský [51] applies the rhodanine base used by F. Feigl [52] to the estimation of traces of *silver* in galenites and flotation concentrates. Procedures are also given [53] for the detection of *germanium* in ores and minerals and in zinc residues. After micro-distillation as the tetrachloride, it is converted into the complex germanium molybdate, which is caused to oxidise benzidine to benzidine-blue, a much-used device in these tests. Certain reactions of germanic acid, *e.g.*, with mannitol, etc., resemble those of boric acid, but are less sensitive.[54] Directions for the detection of many anions are given by N. A. Tananaev and A. M. Schapovalenko.[55] Colour reactions for *iodide*,[56] *nitrite*,[57] elementary *sulphur*,[58] *hydrogen peroxide*,[59] and *ferricyanide* in presence of a large excess of ferrocyanide,[60] have also been described.

By suitable modifications of the Mitscherlich procedure,[61] and of the boric acid–alcohol flame reaction,[62] 0·002 mg. of *phosphorus* and 0·00076 mg. of *boron*, respectively, can be detected.

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[46] *Compt. rend.*, 1932, **194**, 895; *A.*, 1932, 491.

[47] J. V. Dubský and E. Wagner, *Mikrochem.*, 1935, **17**, 186; *A.*, 837.

[48] S. Augusti, *Ann. Chim. appl.*, 1934, **24**, 531; *A.*, 1935, 54. For references see F. Feigl, " Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 1935, p. 259.

[49] E. S. Burkser and M. L. Kutschment, *Mikrochem.*, 1935, **18**, 18; *A.*, 1093.

[50] *Min. Mag.*, 1935, **24**, 21; *A.*, 596.

[51] *Chem. Listy*, 1935, **29**, 133; *A.*, 1093.

[52] *Z. anal. Chem.*, 1928, **74**, 380; *A.*, 1928, 1108.

[53] A. S. Komarovsky and N. S. Poluektov, *Mikrochem.*, 1935, **18**, 66; *A.*, 1095.

[54] N. S. Poluektov, *ibid.*, p. 48; *A.*, 1095.

[55] *J. Appl. Chem. Russia*, 1934, **7**, 1258; *A.*, 1935, 316.

[56] S. Augusti, *Mikrochem.*, 1935, **17**, 113; *A.*, 836.

[57] H. Eichler, *Z. anal. Chem.*, 1935, **100**, 183; *A.*, 463.

[58] A. Schönberg, *Nature*, 1934, **134**, 628; *A.*, 1934, 1321; A. Schönberg and W. Urban, *Ber.*, 1934, **67**, [*B*], 1999; *A.*, 1935, 184.

[59] E. Plank, *Z. anal. Chem.*, 1934, **99**, 105; *A.*, 1935, 52.

[60] E. Storfer, *Mikrochem.*, 1935, **17**, 170; *A.*, 838.

[61] R. Gros, *J. Pharm. Chim.*, 1935, [viii], **22**, 211; *A.*, 1215.

[62] W. Stahl, *Z. anal. Chem.*, 1935, **101**, 342, 348; *A.*, 949.

In the tests which have been mentioned, the limiting amount of an element or ion which can be detected is of the order of 10^{-6} g. or less, and in practically all of them the presence of other constituents necessitates a modified procedure with a resultant loss of sensitivity. For these details, however, the original literature must be consulted.

B. *Drop reactions involving the recognition of crystalline precipitates under the microscope. The Behren's tests.* This line of work continues to be developed. The characteristic crystals formed when picric acid is added to salts of sodium, potassium, ammonium, barium, calcium, magnesium, beryllium, and other metals are described.[63] Crystals of $Zn[Hg(CNS)_4]$ are used for the detection of mercury,[64] and those formed with 2-aminopyridine and sodium bromide or potassium iodide are used for gold, bismuth, and antimony.[65] In a detailed examination, W. F. Whitmore and H. Schneider [66] describe the behaviour of the platinum group and gold with various reagents and select the most characteristic tests. They also give details for the qualitative analysis of the group as a whole. Rhodium yields a yellow crystalline precipitate with ammonium mercuric thiocyanate which serves for its identification,[67] and 1% of cobalt in nickel can be detected by means of pyramidone and ammonium thiocyanate which form characteristic precipitates also with cadmium, cobalt, and some other metals, but not with nickel.[68] Ammonium molybdate can be employed as a microchemical reagent for cerium, aluminium, and certain other elements.[69] The detection of hydrogen cyanide by means of its catalysis of the alloxan–ammonia reaction [70] has been further investigated.[71] Finally, E. M. Chamot and R. W. Brickenkamp [72] have described the characteristic crystalline precipitates which the polythionic acids form with benzyl-ψ-thiocarbamide, nitron sulphate, etc., and have outlined a scheme for the identification of the oxy-acids of sulphur.

Books.—A new edition, revised and enlarged by W. T. Hall, of Volume II (" Quantitative Analysis ") of Treadwell and Hall's text-book has recently been published. The many changes in the text have necessitated a resetting of the entire work.

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[63] C. Frangopol, *Bul. Soc. Chim. România*, 1934, **37**, 259; *A.*, 1935, 949.

[64] I. M. Korenman, *Mikrochem.*, 1935, **16**, 223; *A.*, 318.

[65] A. Sá, *Anal. Farm. Bioquím.*, 1934, **5**, 3; *A.*, 1935, 838.

[66] *Mikrochem.*, 1935, **17**, 279; *A.*, 1096.

[67] A. Martini, *Mikrochem.*, 1935, **16**, 233; *A.*, 319.

[68] *Idem, ibid.*

[69] C. van Zijp, *Pharm. Weekblad*, 1935, **72**, 414; *A.*, 720.

[70] G. Denigès, *Mikrochem.*, 1926, **4**, 149; *A.*, 1926, 1222.

[71] M. T. Koslovski and A. J. Penner, *Arch. Pharm.*, 1934, **272**, 792; *A.*, 1935, 54.

[72] *Mikrochem.*, 1935, **16**, 121; *A.*, 316.

A second edition of Feigl's "Qualitative Analyse mit Hilfe von Tüpfelreaktionen," which rapidly established itself as a standard work, also appeared in 1935. Additional tests for the metals have been included, but the chief feature of the new edition is a section which deals with the application of "spot" tests to organic analysis.

Sutton's "Systematic Handbook of Volumetric Analysis" (Churchill) has been thoroughly revised and brought up to date by A. D. Mitchell. L. S. T.

ORGANIC ANALYSIS.

Modifications and improvements have been suggested for the detection of elements by sodium fusion,[1] the Stepanov[2] and the ter Meulen[3] method of organic analysis, and the rapid determination of carbon by the wet oxidation method.[4]

The following reagents have been investigated for the identification of aldehydes and ketones : *o*-chloro-,[5] *p*-chloro-,[6] 3-nitro-,[7] and *p*-nitro-benzhydrazide,[8] and *o*-tolylsemicarbazide.[9] *p*-Chlorobenzazide[10] has been investigated as a reagent for the identification of primary and secondary amines, whilst 2 : 4 : 6-trinitrobenzoyl chloride,[11] *o*-nitro-, *m*-nitro-, and 3 : 5-dinitro-phenylcarbimides[12] have been investigated as reagents for alcohols.

Mixtures of aromatic nitro-compounds may be rapidly identified by optical crystallographic methods.[13] The crystallographic data for 20 nitro-compounds are described.

The violet-red colour given by a solution of iodine and tannin when poured into a solution of an electrolyte is not due to liberated iodine, as it is also given when the iodine is replaced by chlorine or bromine.[14]

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[1] C. L. Tseng, *J. Chinese Chem. Soc.*, 1935, **3**, 33, 122; *A.*, 876, 1140.

[2] C. L. Tseng, M. Hu, and M. C. Chiang, *ibid.*, p. 223; *A.*, 1258.

[3] J. Gauthier, *Bull. Soc. chim.*, 1935, [v], **2**, 322; *A.*, 506.

[4] C. B. Pollard and W. T. Forsoe, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 77; *A.*, 369.

[5] T. H. Sun and P. P. T. Sah, *Sci. Rep. Nat. Tsing Hua Univ.*, 1934, **2**, 359; *A.*, 1934, 1376.

[6] C. Shih and P. P. T. Sah, *ibid.*, p. 353; *A.*, 1934, 1376.

[7] K. C. Meng and P. P. T. Sah, *ibid.*, p. 347; *A.*, 1934, 1376.

[8] P. Chen, *J. Chinese Chem. Soc.*, 1935, **3**, 251; *A.*, 1259.

[9] H. H. Lei, P. P. T. Sah, and C. Shih, *ibid.*, p. 246; *A.*, 1259.

[10] C. Kao, H. Fan, and P. P. T. Sah, *ibid.*, p. 137; *A.*, 1117.

[11] M. C. Chang and C. H. Kao, *ibid.*, p. 256; *A.*, 1259.

[12] F. Hoeke, *Rec. trav. chim.*, 1935, **54**, 505; *A.*, 958.

[13] E. S. Davies and N. H. Hartshorne, *J.*, 1934, 1830; *A.*, 1935, 102.

[14] F. Allegri, *Boll. chim.-farm.*, 1935, **74**, 555; *A.*, 1244.

Quantitative.—An organic substance may conveniently be estimated by oxidation in 80% sulphuric acid solution by means of a known volume of standard aqueous potassium dichromate solution, the excess of which is determined iodometrically.[15] The iodine values of unsaturated hydrocarbons have been determined by the direct action of bromine vapour.[16] The reaction is complete in 10 minutes, and may be used as a microchemical method.[17] 2 : 4-Dinitrophenylhydrazine has been investigated as a reagent for the determination of carbonyl compounds.[18]

The methods available for the determination of amino-acids have been reviewed,[19] and numerous methods have been described for the determination of individual amino-acids and proteins. The difficulties experienced in the determination of the titratable amino-groups in proteins may be overcome by replacing the mineral acid by either metaphosphoric acid [20] or trichloroacetic acid.[21]

Sugars, with the exception of rhamnose, may be quantitatively precipitated with methyl-alcoholic barium hydroxide solution; [22] they may be recovered from the precipitate by treatment with carbon dioxide, and determined in the filtrate. Reduction of Fehling's solution by invert sugar, but not by glucose, is retarded by Na_2HPO_4 and $Na_4P_2O_7$ to an extent increasing with the duration of the reaction.[23] The interference due to calcium in the volumetric Fehling's titration for invert sugar is eliminated by the addition of sodium hexametaphosphate.[24] An alkalimetric method for the determination of glucose is described,[25] and is claimed to be more accurate than the methods ordinarily employed (0·05% error for 0·1% solutions). By a method based on the oxidation of maltose to maltobionic acid, this sugar may be estimated in the presence of sucrose and monoses,[26] and a method is described for the determination of fructose in the presence of glucose and sucrose.[27]

Colorimetry.—Colour reactions continue to attract considerable attention, in general as specific tests for individual compounds. Such tests are too numerous to record here, but mention is made of certain group reactions. The mono-, di-, and tri-nitro-derivatives of benzene yield with 5% potassium hydroxide solution in acetone, respectively, no colour, a blue, and a blood-red colour.[28] Chloranil gives red, violet, and emerald-green colorations with primary, secondary, and tertiary amines, respectively.[29] Compounds containing CH, CH_2, or CH_3 adjacent to a carbonyl group give red or brown colours with slightly alkaline, alcoholic picric acid,[30] whilst acetic acid and methyl ketones may be detected by the formation of indigotin.[31]

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[15] H. C. S. Snethlage, *Z. anal. Chem.*, 1935, **102**, 321; *A.*, 1390.

[16] E. Rossmann, *Angew. Chem.*, 1935, **48**, 223; *A.*, 728.

[17] J. Böeseken and P. Pols, jun., *Rec. trav. chim.*, 1935, **54**, 162; *A.*, 409.

[18] G. W. Perkins and M. W. Edwards, *Amer. J. Pharm.*, 1935, **107**, 208; *A.*, 998.

[19] O. Fürth, *Sci. Pharm.*, 1934, **5**, 21.

[20] R. K. Schofield, *Trans. Faraday Soc.*, 1935, **31**, 390; *A.*, 300.

[21] R. K. Schofield and L. W. Samuel, *Nature*, 1934, **134**, 665; *A.*, 1934, 1375.

[22] T. Baba, *Biochem. Z.*, 1935, **275**, 253; *A.*, 329.

[23] A. Malkov, *J. Appl. Chem. Russia*, 1934, **7**, 1254; *A.*, 1935, 329.

[24] J. G. N. Gaskin, *Analyst*, 1935, **60**, 318; *A.*, 964.

[25] E. N. Taran, *J. Appl. Chem. Russia*, 1935, **8**, 562; *A.*, 1108.

[26] E. Schapiro and M. N. Proferansowa, *Z. Wirts. Zuckerind.*, 1935, **85**, 196; *A.*, 609.

[27] M. Nordlund, *Suomen Kem.*, 1935, **7**, 95B; *A.*, 1935, 68.

Colorimetric methods are described for the quantitative determination of glycine in proteins,[32] salicylic acid,[33] reducing sugars,[34] total, residual, and polypeptide nitrogen and urea,[35] polypeptides containing a glycyl unit with a free amino-group,[36] tryptophan,[37] cysteine and cystine,[38] nitronaphthalenes,[39] hydroxydimorphine,[40] esters of phytosterol and cholesterol,[41] citral,[42] histidine,[43] quinine,[44,45] and urobilin.[46]

Micro-methods.—The existing apparatus for micro-hydrogenation has been adapted, and, using 1—3 mg. of material, the conditions for the comparisons of the velocity of hydrogenation of different parts of the molecule have been investigated.[47]

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[28] R. W. Bost and F. Nicholson, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 190; *A.*, 877.

[29] J. Siradjian, *Bull. Soc. chim.*, 1935, [v], **2**, 623; *A.*, 769.

[30] M. Goswami, A. Shaha, and B. Mukerjee, *J. Indian Chem. Soc.*, 1934, **11**, 773; *A.*, 1935, 228.

[31] F. Feigl, R. Zappert, and S. Vásquez, *Mikrochem.*, 1935, **17**, 165; *A.*, 877.

[32] A. R. Patton, *J. Biol. Chem.*, 1934, **108**, 267; *A.*, 1935, 370.

[33] J. E. Heesterman, *Chem. Weekblad*, 1935, **32**, 463; *A.*, 1259.

[34] G. A. Bravo, *Boll. Uff. Staz. Sperim. Ind. Pelli*, 1935, **13**, 81; *A.*, 734.

[35] E. Herzfeld, *Mikrochem.*, 1935, **17**, 155; *A.*, 1044.

[36] M. Polonovski, *Compt. rend. Soc. Biol.*, 1935, **120**, 28; *A.*, 1390.

[37] S. Winkler, *Z. physiol. Chem.*, 1934, **228**, 50; *A.*, 1934, 1376; T. Tomiyama and S. Shigematsu, *Proc. Soc. Exp. Biol. Med.*, 1934, **32**, 446; *A.*, 1935, 877.

[38] K. Shinohara, *J. Biol. Chem.*, 1935, **109**, 665; **110**, 263; *A.*, 877; 1110.

[39] B. P. Fedorov and A. A. Spriskov, *J. Gen. Chem. Russia*, 1935, **5**, 450; *A.*, 1116.

[40] B. Drevon, *J. Pharm. Chim.*, 1935, [viii], **22**, 97; *A.*, 1260.

[41] A. Heiduschka and H. Sommer, *Z. Unters. Lebensm.*, 1935, **69**, 75; *A.*, 487.

[42] J. Bougault and E. Cattelain, *J. Pharm. Chim.*, 1935, [viii], **21**, 437; *A.*, 733.

[43] G. Barac, *Compt. rend. Soc. Biol.*, 1935, **118**, 198; *A.*, 370.

[44] G. Denigès, *Bull. Soc. Pharm. Bordeaux*, 1934, **71**, 251; *A.*, 1935, 102.

[45] J. A. Sanchez, *J. Pharm. Chim.*, 1935, [viii], **21**, 24; *A.*, 370.

[46] M. Royer, *Compt. rend. Soc. Biol.*, 1934, **117**, 1240; *A.*, 1935, 379.

Qualitative reactions for monosaccharides,[48] formaldehyde,[49] and nicotine [50] depend on the formation of organic derivatives and the subsequent determination of melting points under the microscope. Flavianic acid is recommended for the isolation and identification of bases. The melting points and the crystallographic and optical characteristics are given for the flavianates of 35 bases, mostly of biological importance.[51] The characteristic reactions for antipyrine,[52] pyramidone,[53] and certain organic acids [54] involve the formation of crystalline precipitates with inorganic reagents. These crystals are distinguished under the microscope by their shape and optical properties. Colorimetric tests have been described for certain compounds of biological interest, the Liebermann–Burchard reaction being extended to include thiophen, furan and derivatives, and carotene.[55]

Volumetric estimations involving the use of the micro-burette have been described for α-keto-acids by the reduction in acid medium of Ce^{IV},[56] for *o*-nitrophenols by means of methylene-blue,[57] and for *n*-butyric acid by an iodometric method.[58] Sucrose has been determined in as little as 5 mg. of solution by the direct measurement of specific gravity and specific rotation,[59] and the carbonyl group may be determined by a method involving the use of a micro-gas burette.[60]

Colorimetric methods have been employed for a variety of substances of biological or pharmacological interest, for methyl alcohol,[61] and for small amounts of organic arsenic compounds in air.[62]

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[47] K. H. Slotta and E. Blanke, *J. pr. Chem.*, 1935, [ii], **143**, 3; *A.*, 862.

[48] R. Fisher and W. Paulus, *Arch. Pharm.*, 1935, **273**, 83; *A.*, 477.

[49] R. Fosse, P. de Graeve, and P. E. Thomas, *Compt. rend.*, 1935, **200**, 1450; *A.*, 877.

[50] R. Fischer and W. Paulus, *Mikrochem.*, 1935, **17**, 356; *A.*, 1141.

[51] W. D. Langley and A. J. Albrecht, *J. Biol. Chem.*, 1935, **108**, 729; *A.*, 639.

[52] M. Wagenaar, *Pharm. Weekblad*, 1935, **72**, 642; *A.*, 877.

[53] *Idem, ibid.*, p. 612; *A.*, 877.

[54] A. J. Steenhauer, *ibid.*, p. 667; *A.*, 998.

[55] V. E. Levine, E. Richman, and G. E. Bien, *Proc. Soc. Exp. Biol. Med.*, 1934, **31**, 582; *A.*, 1934, 1376.

[56] C. Fromageot and P. Desnuelle, *Biochem. Z.*, 1935, **279**, 174; *A.*, 1223.

[57] A. Bolliger, *J. Proc. Roy. Soc. N.S.W.*, 1934, **68**, 51; *A.*, 1935, 1141.

[58] L. Kline, *Biochem. Z.*, 1934, **273**, 1; *A.*, 1934, 1331.

[59] R. Beutler, *Mikrochem.*, 1935, **16**, 133; *A.*, 330.

[60] F. von Falkenhausen, *Z. anal. Chem.*, 1934, **99**, 241; *A.*, 1935, 228.

[61] M. Nicloux, *Bull. Soc. Chim. biol.*, 1935, **17**, 194; *A.*, 1044.

[62] M. Jureček, *Coll. Czech. Chem. Comm.*, 1934, **6**, 468; *A.*, 1935, 101.

Apparatus.—Crucibles containing sintered-glass plates (Schott No. 4) are attacked by alkali and may lose 2—3 mg. when used for weighing cuprous oxide in Allihn's method for determining sugars. The difficulty is overcome by cleaning the crucible in succession with dilute nitric acid, water, alcohol, and ether after use, weighing it, and allowing for the loss.[63]

During distillation, " bumping " is prevented by the presence in the liquid of a sintered-glass disc, through which a stream of air or carbon dioxide is passed.[64] If two right-angled bends 10—15 cm. apart are inserted between the inlet end and the condenser jacket of a Liebig condenser, increased turbulence of the vapours causes more efficient condensation and fewer fractures occur.[65] Apparatus is described for the analysis of organic liquids by fractional distillation,[66] the fractional distillation of small volumes of liquids,[67] and the simple regulation of pressure during a vacuum distillation.[68]

Suggested modifications of the Soxhlet apparatus enable quantitative extraction to be obtained,[69] and an apparatus is described in which the solvent vapour is condensed and allowed to pass through the material at any desired temperature below the boiling point.[70]

R. W. W.

WATER ANALYSIS.

In the decade which has elapsed since water analysis last received mention in these reports, a very large volume of literature has appeared and it will only be possible here to detail some of the more important chemical work. Concurrently, bacteriological methods have also been improved, and the bacteriological examination is still of paramount importance where the hygienic quality of the water is under consideration.

Various attempts have recently been made to devise some roughly quantitative method of estimating the intensity of the taste and odour of water. The maximum dilution in which a taste or odour is still apparent is termed the " threshold value," [1] and dilution is best performed with water which has been completely deodorised with activated carbon.[2] An alternative method of measurement is by means of the " osmoscope," in which definite dilutions of the

[63] P. Balavoine, *Mitt. Lebensm. Hyg.*, 1935, **25**, 323; *A.*, 599.

[64] M. Mattikow, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 136; *A.*, 599.

[65] H. Schanz, *Chem.-Ztg.*, 1935, **59**, 458; *A.*, 952.

[66] H. S. King, *Proc. Nova Scotian Inst. Sci.*, 1934, **18**, 272; *A.*, 1935, 1098.

[67] W. Swientoslawski, *Rocz. Chem.*, 1934, **14**, 614; *A.*, 1935, 321.

[68] O. J. Schierholtz, *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 284; *A.*, 1098.

[69] A. G. Kuhlmann, *Z. Unters. Lebensm.*, 1935, **69**, 221; *A.*, 724.

[70] F. W. Neumann, *Chem. Fabr.*, 1935, **8**, 326; *A.*, 1218.

[1] C. H. Spaulding, *Amer. J. Public Health*, 1931, **21**, 1038.

[2] O. Gullans, *J. Amer. Water Works Assoc.*, 1933, **25**, 974.

odour with air may be arranged. The intensity of odour is then denoted by the number of times (p_0) that the odour must be diluted with an equal volume of odourless air in order to reach the threshold value.[3]

The discovery that extremely minute quantities of phenols are liable to give rise to taste in chlorinated water has stressed the need for accurate methods for their determination. J. R. Baylis[4] has based a method on the Gibbs indophenol test (blue coloration with quinone-chloroimides), the actual reagent employed being 2 : 6-dibromoquinone-chloroimide. The p_H of the solution is an important factor and should not vary by more than 0·2 unit either way, so all test solutions must be highly buffered. By use of a suitable distillation technique, the method is claimed to be capable of determining 1 part of phenol in 1000 million parts of water. Several workers[5] have also employed colorimetric methods based on the coupling of the phenol with diazotised *p*-nitroaniline. The method is sensitive to 0·05 part of phenol per million, although smaller concentrations may be determined if the phenol is first concentrated by distillation.

Attention has been paid to the *o*-tolidine method of determining free chlorine in water, and a study has been made of the possible interfering substances. Experiments[6] show that the formation of the yellow colour with the reagent is probably due to oxidation rather than chlorination, and that chloroamines may also produce the colour although more slowly (10—20 minutes) than chlorine. Nitrites and tervalent manganese or iron also give a yellow colour with the reagent. Manganic salts do not interfere if previously reduced to the bivalent state by addition of a dilute solution of hydrogen peroxide,[6] or alternatively[7] they may be removed by coprecipitation with magnesium hydroxide. It is stated[8] that, although free chlorine and nitrite cannot co-exist for long in distilled water, chloroamine and nitrite can exist simultaneously in neutral, but not in acid, solution.

Interference of nitrite may be prevented by a preliminary treatment with hydrogen peroxide,[9] or a suitable correction factor may be applied to the *o*-tolidine indication.[7] The use of four times the concentration of hydrochloric acid normally employed in the test prevents interference of ferric salts.[10]

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[3] G. M. Fair and W. F. Wells, *Water Works Eng.*, 1934, **87**, 1051.

[4] *J. Amer. Water Works Assoc.*, 1928, **19**, 597.

[5] S. Hilpert and R. Gille, *Angew. Chem.*, 1933, **46**, 326; Nolte, *Chem.-Ztg.*, 1933, **57**, 654; T. Folpmers, *Chem. Weekblad*, 1934, **31**, 330; *B.*, 1934, 606.

[6] H. W. Adams and A. M. Buswell, *J. Amer. Water Works Assoc.*, 1933, **25**, 1118.

[7] R. D. Scott, *ibid.*, 1934, **26**, 634.

[8] D. Tarvin, H. R. Todd, and A. M. Buswell, *ibid.*, p. 1645.

[9] C. H. H. Harold, *Ann. Report of Director of Water Examination, M.W.B.*, 1934, p. 4.

It is noteworthy that more than 0·2 part per million of free chlorine produces a pink coloration in the *m*-phenylenediamine test for nitrites.[11]

New tests for nitrites in water depend on the blue coloration produced with neutral-red,[12] and the yellow coloration with benzidine; [13] also on the orange coloration formed on boiling with 2 : 6-di-iodophenolsulphonate, and the red colour after boiling with catechol and then rendering alkaline.[14]

In distilling off free ammonia from polluted waters, it has been shown that addition of sodium carbonate before distillation may cause hydrolysis of organic nitrogenous compounds. It is therefore preferable to substitute a phosphate buffer solution which maintains a constant p_H of 7·4 throughout the distillation. The ammonia is then recovered quantitatively and the hydrolytic action is minimised.[15]

It is still a fact that the methods available for the chemical examination of the organic matter in waters are somewhat empirical. An attempt has been made by J. W. Haigh Johnson [16] to correlate the " oxygen absorbed " and the " albuminoid ammonia " test by means of an " oxy-albuminoid " method. In this method, the sample, after removal of free ammonia, is refluxed with a standard alkaline permanganate solution for 30 minutes. Aliquot portions are then taken, and the unreduced permanganate and the albuminoid ammonia are determined. The oxygen absorbed from permanganate in this method is stated to be about four times that absorbed from acid permanganate, and is therefore in closer agreement with the biological oxygen demand. Moreover, the albuminoid ammonia is quickly distilled and definite in amount.

The urease method has now been applied to the determination of urea in water, and a technique has been described by which 0·004—0·200 mg. of urea may be determined. According to M. H. McCrady,[17] the present evidence indicates that urea in water is specific proof of excretal pollution.

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[10] R. D. Scott, *J. Amer. Water Works Assoc.*, 1934, **26**, 1234.

[11] J. C. Harral and F. W. M. Jaffé, *Analyst*, 1932, **57**, 308; *B.*, 1932, 641.

[12] M. S. Vergnoux, *Ann. Chim. analyt.*, 1929, **11**, 366.

[13] G. Carpentier, *Union Pharmaceut.*, 1932, **72**, 162; *Chem.-Zentr.*, 1932, [ii], 3761.

[14] A. Castiglioni, *Gazzetta*, 1932, **62**, 1065; *A.*, 1933, 243.

[15] M. S. Nichols and M. E. Foote, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 311.

[16] *Analyst*, 1927, **52**, 130.

[17] *J. Amer. Water Works Assoc.*, 1930, **22**, 926.

The test for the biological oxygen demand of polluted waters has continued to receive attention, particularly in America. The character of the water used for dilution in the test is an important factor in obtaining concordant results. Current American practice [18] employs distilled water which is buffered with 0·03% of sodium bicarbonate and does not absorb more than 0·2 part per million of dissolved oxygen in 5 days at 20°. The p_H of the sample is best adjusted before dilution to fall between 6·5 and 9·0, and the dilution in which the oxygen has been depleted nearest to 60% of the original content is recommended [19] for the calculation of the oxygen demand.

A rapid method for the estimation of dissolved oxygen is based on the production of a reddish-brown colour with amidol. Solutions of potassium citrate and of amidol are added to the sample in a stoppered tube, and the colour is matched against permanent standards prepared from solutions of cobalt chloride and potassium dichromate.[20]

G. W. Hewson and R. Ll. Rees [21] have applied the electrical "dead-stop" end-point method [22] to the titration of the small amounts of iodine liberated when determining the dissolved oxygen in de-aerated waters by the Winkler method. For these low iodine concentrations the starch-iodide end-point is not sufficiently sensitive. The electrical method depends on the fact that if two platinum electrodes having a small potential difference (15 mv.) are immersed in the solution during the thiosulphate titration, the cathode becomes completely polarised at the end-point and no current then passes. A back titration technique is described whereby variations of iodine concentration equivalent to 0·001 ml. of oxygen per litre may be detected.

In the Winkler method for the determination of alkaline hydroxides in the presence of carbonate and sulphate, the precipitate of barium sulphate is liable to cause considerable error by occluding hydroxide. The error is minimised if strontium chloride is used in place of barium chloride,[23] but the solution then requires boiling before subsidence and subsequent titration of the supernatant liquid.

Various volumetric methods for the determination of sulphate in water have been described in recent years and among these are modifications of the well-known barium chromate method.[24] Alternatively, the sulphate may be precipitated with standard barium chloride, excess of which is titrated with sulphuric acid using sodium rhodizonate as internal indicator,[25] or with an alcohol–glycerol solution of potassium palmitate using phenolphthalein.[26] An approximate method has also been based on the reaction of sulphate with a suspension of barium carbonate, the sodium carbonate produced being titrated.[27] Volumetric methods of sulphate determination are especially valuable in the routine analysis of boiler water, and a critical examination of the various methods [28] indicates that the palmitate method is most suitable for this purpose.

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[18] "Standard Methods for the Examination of Water and Sewage," American Pub. Health Assoc., 1933, p. 89.

[19] 6th Annual Report, Ohio Conference on Sewage Treatment, 1932, 61, Appendix III; see Water Pollution Research Abstract, 1934, No. 983.

[20] M. L. Isaacs and F. W. Gilcreas, *Sewage Works' J.*, 1935, **7**, 435; *B.*, 928.

[21] *J. Soc. Chem. Ind.*, 1935, **54**, 254T; *B.*, 832.

[22] C. W. Foulk and A. T. Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045.

[23] W. C. Schroeder, *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 389; *B.*, 1934, 47.

According to L. A. Thayer,[29] the colorimetric method of F. Diénert and F. Wandenbulcke (*Compt. rend.*, 1923, **176**, 1478) for the determination of silica by conversion into silicomolybdate is inaccurate if appreciable amounts of iron or phosphate are present. In such cases a preliminary procedure is recommended in which iron is removed as ferric phosphate in acetic acid solution and the excess phosphate is precipitated as calcium phosphate. The filtrate is then tested for silica by the colorimetric method.

A survey of the methods of testing for traces of cyanides in water has shown [30] that the best procedure is to distil it with tartaric acid (under reduced pressure if phenols, fatty acids, etc., are present) and then to examine the distillate. The Prussian-blue test is, of course, specific for cyanide in the absence of ferrocyanide, and it is recommended when the concentration of hydrogen cyanide is over 1 in 250,000. For lower concentrations, it is advisable to employ the nephelometric silver cyanide method or the colorimetric method based on the production of phenolphthalein from the phthalin in the presence of cyanide and a trace of copper. Neither the silver cyanide nor the phenolphthalein method is, however, specific.

The determination of small quantities of fluoride in water has recently assumed prominence owing to the probable association of fluorine with mottled tooth-enamel. For this purpose H. V.

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[24] G. Nachtigall and F. Raeder, *Arch. Hyg.*, 1928, **100**, 31; R. Schmidt, *Z. anal. Chem.*, 1930, **82**, 353.

[25] B. Paschke, *Z. Unters. Lebensm.*, 1931, **62**, 378; *B.*, 1932, 50.

[26] P. Hamer, *J. Soc. Chem. Ind.*, 1935, **54**, 250T; G. Ammer and H. Schmidtz, *Vom Wasser*, 1933, **7**, 185.

[27] D. Northall-Laurie, *Analyst*, 1931, **56**, 526; *B.*, 1931, 909.

[28] H. Reichelt, *Chem.-Ztg.*, 1934, **58**, 871.

[29] *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 276; *A.*, 1930, 1145.

[30] A. E. Childs and W. C. Ball, *Analyst*, 1935, **60**, 294; *B.*, 656.

Churchill[31] has employed the volumetric method in which the fluoride is converted into ferric fluoride by the addition of standard ferric chloride solution, the excess of which is determined iodometrically. Several workers[32] have also applied the de Boer zirconium–alizarinmonosulphonate reagent to this problem. The reddish-violet colour produced by this reagent in acid solution is discharged by traces of fluorine, and a technique has been described by Barr and Thorogood whereby 5 parts of fluorine per million may be determined directly to within 0·1 part. Calcium, iron, sulphate, phosphate, and organic matter are, however, all apt to interfere, and for greater accuracy it is preferable to distil the fluorine as silicon tetrafluoride and apply the test to the distillate,[33] or to employ standards of similar composition to the sample.[34] The test may be made more delicate by the use of quinalizarin[35] or purpurin[36] in place of alizarin.

The quantity of iodide present in natural waters is usually extremely small, and it is necessary to employ very large samples (preferably 25—100 litres) for its determination. J. J. Hinman[37] recommends that the solids obtained by evaporation should be ignited, with precautions to avoid losing iodine, which is then liberated by addition of nitrosylsulphuric acid, extracted with carbon tetrachloride, and matched against standards. In Martindale's method,[38] the iodide is extracted from the solids with 95% alcohol, and the iodine liberated with nitrous acid and matched in ethereal solution.

A method for the determination of lead in waters containing iron, copper, and organic matter has been based on its adsorption on calcium carbonate.[39] Potassium cyanide is added, and the sample shaken for an hour with the calcium carbonate, which is then filtered off and dissolved. The solution is treated with ammonium persulphate to oxidise organic matter, iron is reduced with hydrazine dihydrochloride, and the lead then determined by the usual colorimetric (Winkler) method.

The white precipitate produced by zinc with sodium diethyldithiocarbamate may be used for the turbidimetric determination of traces of the metal in water.[40] The reagent is stated to be as sensitive as ferrocyanide.

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[31] *Ind. Eng. Chem.*, 1931, **23**, 996.

[32] E. Elvove, *U.S. Pub. Health Reports*, 1933, **48**, 1219; J. M. Sanchis, *Ind. Eng. Chem.* (*Anal.*), 1934, **6**, 134; G. Barr and A. L. Thorogood, *Analyst*, 1934, **59**, 378.

[33] C. S. Boruff and G. B. Abbott, *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 236.

[34] Barr and Thorogood, *loc. cit.*, ref. (32).

[35] O. M. Smith and H. A. Dutcher, *ibid.*, 1934, **6**, 61.

[36] I. M. Kolthoff and M. E. Stansby, *ibid.*, p. 118.

[37] *J. Amer. Water Works Assoc.*, 1928, **19**, 566.

[38] " Extra Pharmacopœia," 1929, Vol. II, 424.

[39] J. F. Reith and J. de Beus, *Chem. Weekblad*, 1935, **32**, 205; *B.*, 527.

For the determination of very small quantities of silver (*e.g.*, in waters disinfected by oligodynamic action), the metal may be matched colorimetrically after addition of Rochelle salt and sodium sulphide.[41] In a further method[42] the silver is filtered off as iodide through a membrane of porosity 1μ, an aqueous solution of hydrogen sulphide passed through the membrane, and the density of the resulting coloration of the membrane compared with standards. It is claimed that 0·0025 part of silver per million may be determined in this way if sufficiently large samples are examined with a membrane of small area. It has, however, been maintained[43] that the only reliable method of determining the strength of an oligodynamic water is by comparing its bactericidal action against a standard silver solution prepared by shaking distilled water with silver oxide.

It seems likely that the application of micro-methods to the chemical examination of water may well offer considerable advantages in certain cases. C. Urbach[44] has recently described various photometric micro-methods for the analysis of water. It is stated that nitrates, nitrites, ammonia, magnesium, calcium, sulphate, phosphate, silicate, lead, and iron may all be determined in this way.

G. U. H.

G. U. Houghton.
L. S. Theobald.
R. W. West.

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[40] W. R. G. Atkins, *Analyst*, 1935, **60**, 400; *B.*, 752.

[41] Chlorator-G.m.b.H., Swiss P., 171,766; *Chem. Zentr.*, 1935, **i**, 3455.

[42] J. Just and A. Szniolis, *Arch. Chim. Farm.*, 1935, **2**, 170; *A.*, 719.

[43] F. Eichbaum, *Zentr. Bakt. Par.*, Abt. I, 1932, **126**, 152.

[44] *Mikrochem.*, 1932, **10**, 483; **11**, 37, 50; 1933, **13**, 31, 201; 1934, **14**, 189, 198, 321, 331; **15**, 207; *B.*, 1932, 658; 1933, 494, 734; 1934, 430, 654, 1038.

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